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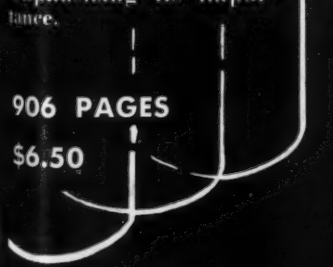

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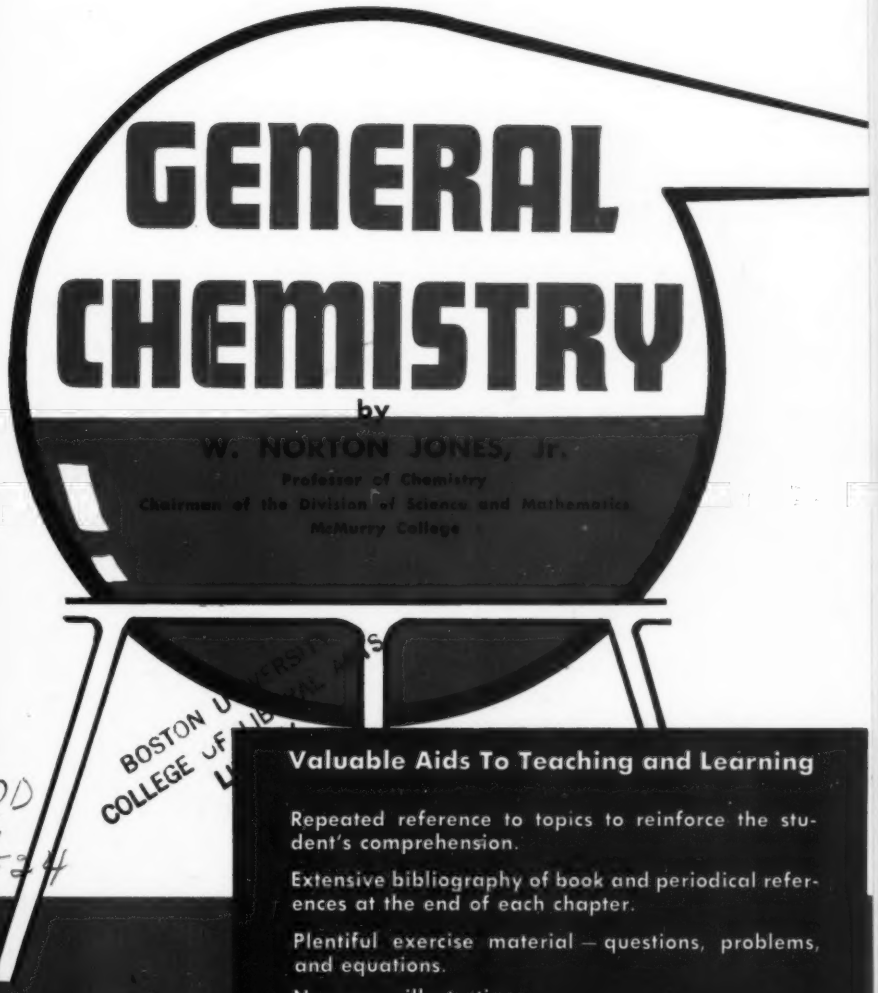

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5. STATES OF MATTER. SOLUTIONS.

A. THE THREE STATES: GASEOUS, LIQUID, SOLID

*5-1 *Change of state.* Moth balls, ice cube, burner, 3 test tubes, 10-g. weight. **Put four moth balls in each of two tubes; melt moth balls in one tube, showing a watery-like liquid forms with some naphthalene vapor noticeable, but resolidifies into white naphthalene. Melt ice until tube is half-full of liquid, slide in weight to hold down the ice, and boil water at top of tube: illustrates the three states of matter.**

*5-2 Models showing relative emptiness of matter. See footnote.

B. THE GASEOUS STATE

5-3 **Exhibit:** mercury barometers, diaphragm barometers.

5-4 Torricelli-type barometer tube immersed in a beaker of Hg and passing through one-hole rubber stopper inserted in large bell jar which is attached to a vacuum pump, oil or water type. **Evacuate, showing fall of mercury level. If water aspirator is used, show mercury level does not fall below the vapor pressure of water at room temperature.**

5-5 See 3-11, diffusion of hydrogen experiment, ringing bell and making a fountain.

5-6 Extension cord with resistance wire of such resistance that it glows dull red with 110 volts A.C. Beakers of dry ice, air, hydrogen. **Show that wire glows brighter in CO_2 than in air, but duller in H_2. Discuss motion of molecules, diffusion of heat, operation of Pirani gauge.**

5-7 Neon tube, a high frequency "leak tester," 3-ft. length of 10 mm. glass tubing with a tiny leak in its "closed" end, and with the other end fastened by rubber pressure tubing to a vacuum pump. **Test for leaks before and after pump is operated. Light the neon tube. Discuss principle of electric discharge in gases at a few mm. pressure.**

C. THE LIQUID STATE. SOLUTIONS

Types of Solutions

*5-8 *Formation.* $AgNO_3$-aq., 1% fresh gelatin solution, conc. HCl, 2 test tubes. **Add 2 drops HCl to (a) 25 ml. gelatin solution in one tube, and (b) 25 ml. water in other tube. Then add a few drops $AgNO_3$-aq. Colloidal AgCl forms in tube (a) only.**

5-9 *Filterability.* $CuSO_4$-aq., $NiSO_4$-aq., muddy water, colloidal AgCl, colloidal $Fe(OH)_3$. 5 test tubes in rack, 5 funnels with filter paper. Cellophane bags of $CuSO_4$-aq. and colloidal $Fe(OH)_3$ suspended in beakers of water day before lecture. **Filter through paper, showing that both true solutions and colloid suspensions run through but that only $CuSO_4$ runs through the semi-permeable cellophane membrane.**

5-10 *Tyndall cone.* Solutions from 5-9. Powerful pencil of light, as from a slide projector with cardboard slide with a $^1/_4$" hole in its center. **Place bottles of true solutions and colloidal suspensions in beam, showing Tyndall cone for latter.**

Solutions of Gases

5-11 Dry ice, NH_3 tank with rubber tubing, two 2-liter cylinders of water. **Show that the CO_2 bubbles increase in size as they rise, but the NH_3 bubbles grow smaller as the NH_3 dissolves.**

*5-12 *HCl or ammonia fountain.* See Figure 5-12. A 6mm tubing, 30 cms. long, with stopcock, passing through a two-hole rubber stopper inserted in a 1-liter *round-bottom* Florence flask with the tubing leading to the bottom of

Turn the page for additional demonstrations

*Footnotes

5-1 Tube may crack unless flame is kept below water level.

5-2 Make the following models. (a) A $^1/_2$-oz. clear glass bottle containing 56 g. (1 g. atomic weight) of steel BB, shot. (b) A 1 oz. clear glass bottle containing 18 ml. (1 g. mole) of water; on the cap a model of H_2O attached, scale 1 cm. = 1 Ångstrom. (c) A bottle, about 22.4 liters capacity inside which is suspended on a string a dumb-bell model of O_2, scale 1 cm. = 1 Ångstrom. These models represent a mole of each material and/or the space they have to move around in, at the scale indicated.

5-8 If time permits, boil the two solutions; the mixture without gelatin rapidly coagulates.

5-12 The use of indicators is interesting, although it may confuse the student. It might be well to perform without indicators the first time it is done, later to use indicators. With the HCl-fountain the use of methyl violet indicates very clearly that the first few drops of water dissolve most of the HCl, since the solution becomes bright yellow at the very beginning of the fountain, later green to blue to violet spreading throughout the flask. Phenolphthalein can be used with the NH_3-fountain.

Use only a round-bottomed flask; a flat-bottomed flask will often collapse as soon as the vacuum is established.

5-13 This gives the lecturer an opportunity to refresh himself, to the amusement of the class and the profit of the lecturer.

5-14 Where local option permits, mention the significance of such phrases as "86 proof"!

5-15 **CARE.** Be sure that the ether bottle and the separatory funnel containing ether are taken a good distance away before lighting the match and throwing it on the tray of ether-in-water. Also, the $CuSO_4$ imparts a greenish color to the burning ether.

Labels for Topic 5. (For code, see instructions for assembling kits, *J. Chem. Educ.* **32**, 12A(1955).) 5-1-*J*-moth balls, 5-4-*N*-Hg, 5-8-*d*-$AgNO_3$, 5-8-*w*-gelatin, 5-8-*d*-conc. HCl, 5-9-*N*-$CuSO_4$ aq., 5-9-*N*-$NiSO_4$ aq., 5-9-*N*-muddy water, 5-9-*N*-colloidal AgCl, 5-9-*N*-colloidal $Fe(OH)_3$, 5-9-*J*-cellophane bags, 5-10-*N*-$CuSO_4$ aq., 5-10-*N*-$NiSO_4$ aq., 5-10-*N*-colloidal AgCl, 5-10-*N*-colloidal $Fe(OH)_3$, 5-12-*d*-phenolphthalein solution, 5-12-*d*-methyl violet solution, 5-14-*N*-ethanol, two labels for 5-15-*N*-ether, 5-15-*N*-$CuSO_4$ aq., 5-16-*w*-cork stoppers, 5-16-*w*-1" length of candles, 5-16-*w*-1" length rubber tubing, 5-16-*w*-Pb tubing, 5-16-*w*-Pt foil, two labels for 5-16-*N*-CS_2, two labels 5-16-*N*-ether, two labels 5-16-*N*-Hg, 5-17-*w*-wax, 5-17-*w*-$KMnO_4$, 5-17-*N*-NaCl, 5-18-*J*-KNO_3, 5-18-*w*-$Ca(OH)_2$, 5-19-*J*-NaCl, 5-19-*w*-NaCl pellets, 5-19-*d*-phenolphthalein, 5-20-*J*-NaCl, two labels for 5-21-*J*-sodium thiosulfate, 5-21-*w*-NaCl, 5-21-*J*-cotton.

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the flask; in the other hole of the stopper, a medicine dropper containing a small amount of water. The flask is to be completely filled with ammonia or HCl gas and inverted in a ring on a stand so that the lower end of the tubing extends to the bottom of a 1500 ml. beaker nearly full of water. **Open the stopcock. CARE: PROTECT FACE AGAINST FLASK COLLAPSING. If necessary squeeze some water out of the medicine dropper into the flask: water rushes into the inverted flask making a fountain.**

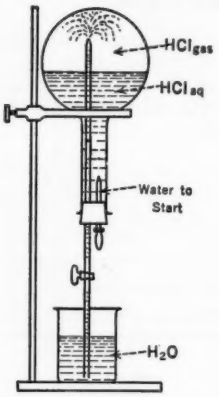

Figure 5-12

*5-13 Three 250 ml. beakers. Three Coca Cola bottles (a) uncapped, in a beakerful of cracked ice, (b) uncapped, at room temperature overnight, (c) capped. **Show more CO_2 foam from Coca Cola at lower temperature or higher pressure.**

Solutions of Liquids

*5-14 *Miscible.* Alcohol, 2 test tubes. **Show that alcohol-water mix in all proportions.**

*5-15 *Partially miscible.* Ether, $CuSO_4$-aq., 1-, liter separatory funnel in ring with stand, glass tray about 18 × 10 × 2″. **Shake about 200 ml. ether with 500 ml. water. Show it forms a water-in-ether and an ether-in-water layer: add $CuSO_4$-aq. to make the water layer more distinct. Run water layer out of separatory funnel into the glass tray. Remove the separatory funnel still containing the ether layer. CARE: throw a lighted match on the ether-in-water layer in the glass tray.**

5-16 *Immiscible.* 1-liter cylinder; small pieces of cork, candle, rubber tubing, Pb, Pt foil; 200 ml. each of CS_2, Hg, ether, water. Form layers of Hg, CS_2, water, and ether in that order. **Drop in Pt (crumple up foil into a ball), Pb, rubber, candle, cork in that order. Forms four liquid layers with the solids seeking proper density levels. Illustrates immiscibility and density differences.**

Solutions containing solids

5-17 $KMnO_4$, 1-liter cylinder of water, 1-liter cylinder containing saturated brine with excess solid salt on bottom, 2 clock-glasses, wax. Put drop of wax on the convex surface of each clock-glass; push into the wax a crystal of $KMnO_4$. **Having both cylinders filled to the brim, invert clock-glasses on them. Observe $KMnO_4$ dissolving in water, and in a solution already saturated with brine (Query: will $KMnO_4$ dissolve if the solution is already saturated with brine?)**

5-18 Two 250 ml. beakers, over burners, KNO_3, $Ca(OH)_2$, 2 stirring rods. **Solubilities at 0°/100°C in 100 g. water are KNO_3 13/246, and $Ca(OH)_2$ 0.19/0.08. Demonstrate this by dissolving 50 g. KNO_3 and 0.2 g $Ca(OH)_2$ in 200 ml. water each; then heat.**

Strength of solution

5-19 *Molar and normal.* Burette, phenolphthalein solution; volumetric flasks, including one of 1-liter capacity; NaCl, NaOH flakes or pellets, a $2^1/_2$ liter carboy of conc. H_2SO_4 with label showing % composition of H_2SO_4. **Explain how to make up a 1-M and a 1-N solution of NaCl and of H_2SO_4. Explain use in titration using a burette. Explain that 1 Normal solution contains 1 mole of available H^+, of OH^-, or of electrons per liter.**

5-20 *Molal.* Balance, weights and filter paper; volumetric flask calibrated to hold and to deliver 1000 ml.; freezing-point apparatus; NaCl. **Explain how a 1 molal solution is made up, as contrasted to molar or normal solutions. Explain use of molal concept in F.P. depression measurements.**

5-21 *Degree of saturation.* Two 1-liter Florence flasks, cotton, NaCl, 1 kg. sodium thiosulfate (photographers' hypo). Melt the hypo in flasks, protect mouths of flasks with cotton. **Drop NaCl crystal into one flask: no crystallization occurs. Drop hypo crystal into the other: crystallization occurs, because the supersaturated solution has been seeded with a crystal of the correct lattice.**

D. THE SOLID STATE

5-22 **Exhibit**: mineral crystals, alums, alloys, metallographic samples showing etched surfaces.

5-23 **Exhibit**: atomic and molecular models.

Next month's Tested Demonstrations in General Chemistry

6. IONIZATION

For a complete list of topics for 1955–6 see J. Chem. Educ., 32, 28–9(1955)

Athanasius Kircher, S.J.

(See page 253)

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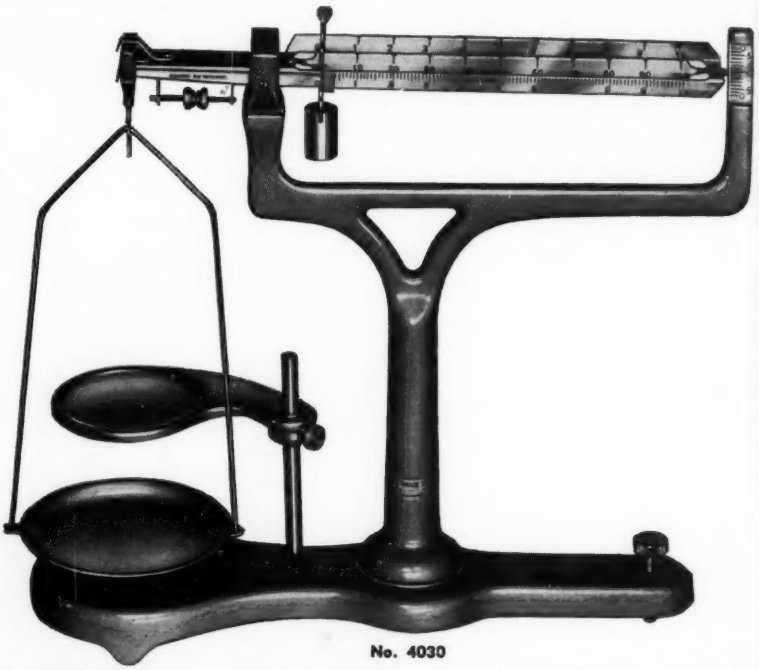

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Editor's Outlook

THERE is every reason to think that the country is facing a crisis; indeed it may be that the crisis will erupt into something worse before this appears in print. Under the circumstances it would be well for us to take stock of all our resources. We have a good measure of military strength, if we should need it; we have material wealth, a stable economy, and enormous industrial potential; we have at least a small circle of international friends—enough to furnish among us a dubious minimum of manpower. But all these are of no avail without the most important element: a highly developed technology based upon brainpower and intellectual leadership. It is worth noting and remembering that democracy can only be preserved by the few that stand out among the crowd. If that be snobbery, make the most of it. What removes the stigma from this kind of neo-aristocracy is the fact that anyone can become one of the elite if he has what it takes to rise to that estate. Indeed, the more we can elevate, the better for us all.

What this all means, of course, is that we are dependent upon our ability to discover and develop the brilliant minds in our younger generation. Unfortunately, our school administrators, while not entirely oblivious to this, are largely preoccupied with plans for the mediocre and mentally retarded. We should have proportionally as many special classes for the superior as for the subnormal. Do we leave our diamonds and solid gold lying around on the floor, because they will not rust in any event, while we spend all our time polishing the brass?

One of the most stimulating group discussions at the recent meeting of the National Science Teachers Association, which I had the pleasure of attending, was that which concerned means for dealing with superior students. It was proposed to call these gifted youngsters by the more modest term "rapid learners"—in order, I suppose, to avoid the danger of invidious comparisons. While this may be good politics, I can see no reason to be apologetic about the fact that some people are brighter than others. I confess I have many friends whose stellar magnitude is brighter than mine, and I don't lose any sleep over it. Surely, this is one of the facts of life which we must all learn.

It is encouraging that here and there something special is being done for the gifted student, but teachers seem to feel almost guilty about stealing the time from their slower pupils. Science fairs and the Westinghouse Science Talent Search are of course among the best organized efforts in this direction, but local communities and individual teachers can do much also. The important thing is to eliminate the feeling that the bright boys and girls do not need any help but will take care of themselves. Far from its being undemocratic to single them out for special attention, it is on the contrary undemocratic to deny them the opportunity to make the very best of themselves. If they don't, we won't have much democracy left.

While this problem is most acute at the secondary-school level, nevertheless it exists in somewhat different form in the college or university. The term "intellectual snob" is occasionally heard, and sometimes with deserved opprobrium. But the superior student is usually appreciated and generally marked for special attention. However, the distinction is sometimes between the undergraduate and graduate levels. I know one large university which feels it best to say as little as possible about its graduate research program, because the state legislature cannot understand this as well as it can undergraduates. "The Lord must love the common man, he made so many of them."

RECENT ADVANCES IN PETROCHEMICALS[1]

THEODORE W. EVANS
Shell Development Company, Emeryville, California

In discussing recent advances in petrochemicals, it is convenient to take for the period under review the time which has elapsed since the end of World War II, or, in other words, about the last eight years. This choice is made so that a sufficient period is covered to show some of the significant trends of this industry and, if possible, draw conclusions as to what may be expected in the future. Actually, the industry itself is only about thirty years old, so that even this relatively short period we are reviewing does cover about one-quarter of its existence.

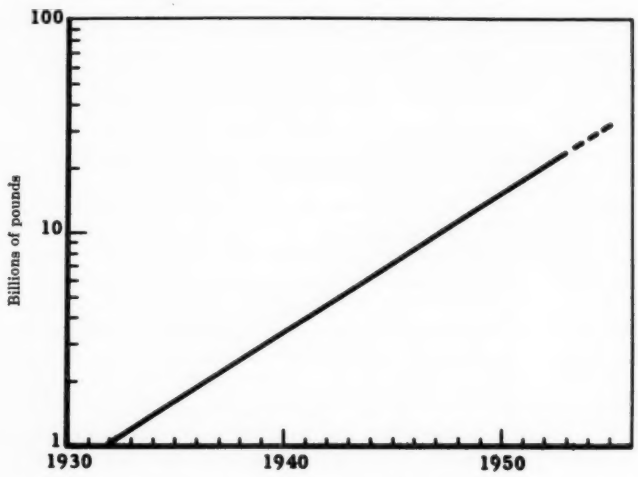


Figure 1. U. S. Petrochemical Production

In examining what has happened during these past eight years, one is immediately struck by several things, notably the rapid growth and diversification, the increasing importance to the national economy, and the price stability which has been brought to a number of major commodities. The over-all growth of the industry is shown in Figure 1. At the present time its production is divided roughly into 65 per cent aliphatics, 10 per cent aromatics, and 25 per cent inorganics. In total it now amounts to one-fourth the production and one-half the value of the entire chemical industry. The remarkable rate of growth of petrochemicals is quite obvious. When expressed in numbers the average yearly increase for this industry has been about 15 per cent, as compared to 10 per cent for the chemical industry as a whole and 3 per cent for all industry. Basically this growth has been the result of a number of factors: an abundant supply of raw material, an aggressive policy of research and development, and a willingness to invest money, all superimposed on a generally expanding industrial economy. Plant expansion and technologic improvements enabled the industry in a number of cases to maintain relatively stable prices in the face of generally inflated cost. This is illustrated in Figure 2, where the prices of ammonia and formaldehyde are plotted against time, and for comparison the relative purchasing power of the dollar is shown. In many ways it is a remarkable tribute to this industry that it has been able to maintain such a price history during a period of general inflation of values.

In looking at the technical details of the industry, several aspects are immediately apparent. First, a number of existing processes have been subject to continuous improvement which, while not revolutionary, has nevertheless been of great over-all benefit in maintaining the favorable price history just mentioned. Second, a number of new processes have appeared for existing products. These again have aided the price picture and are illustrative of the high degree of competition within this industry, or even within a single company, where the endeavor is always to do things better and cheaper. Third, a few petrochemicals have become the source of numerous derivatives during the period under review, and finally, many new derivatives have been offered to the trade, of which a number are finding a permanent place in our economy.

IMPROVED TECHNOLOGY ON OLDER PETROCHEMICALS

A number of basic older petrochemicals have, since the war, undergone significant improvement in process or product quality, or both. These include ammonia, carbon black, ethyl, isopropyl, and butyl alcohols, and ethylene oxide, which combined represent a large part of prewar petrochemicals volume. Individual improvements in each of these older processes and products are not generally spectacular, but combined they can account for large steps forward.

In the ammonia field the great change has been the shift toward natural gas as a more economic raw material. This can be illustrated by noting that while ammonia capacity based on coke has declined somewhat since the war, capacity based on natural gas has approxi-

[1] Presented at the Symposium on Recent Advances in Petroleum Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, March, 1954.

mately doubled. The cumulative effect of other economies cannot be neglected, however. The average plant size is about four times the prewar figure. Reduction in compressor cost is reported for manufacture of the required hydrogen under pressure. The impact of postwar, low-cost air fractionation appears in ammonia technology with reforming of methane by partial combustion, and in the continuous manufacture of water gas from coke in preference to the older cyclic procedure using air. Use is made also of liquid nitrogen for removal of contaminants from the feed gases to the ammonia synthesis reactors. Catalyst improvements have been adopted and continuous plant control of methane, argon, and trace concentrations of carbon oxides provides the necessary safeguards for optimum operation with a high on-stream factor and minimum waste of manpower.

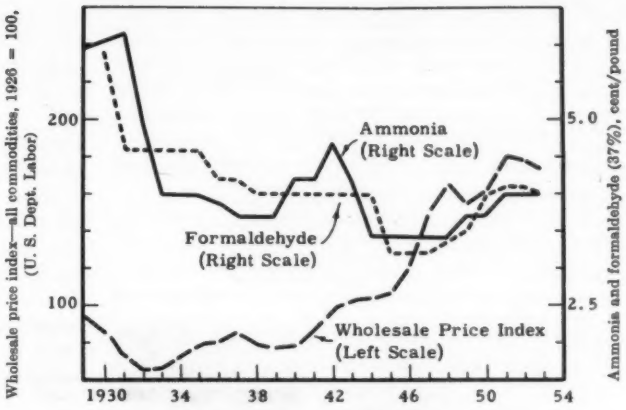


Figure 2. Price History of Selected Petrochemicals

In the carbon-black field the great change has been the decline in importance of the channel blacks and the rise of the furnace blacks as shown in Figure 3. This change has occurred because of the problems associated with synthetic rubber. Channel black is an excellent reinforcing agent for natural rubber, but is only moderately satisfactory with today's synthetic material. This deficiency led to a great deal of research looking for improved reinforcing agents for synthetic rubber, and from this work the so-called super-abrasion furnace blacks resulted. Figure 3 shows how successful the furnace blacks have been, and to what an extent they have captured business from the channel blacks. An increasing amount of heavy, highly aromatic petroleum oil has been consumed in the manufacture of these furnace blacks. As of today, about half the furnace black is derived from natural gas and half from these heavy petroleum fuels. From the standpoint of raw-material consumption, the furnace process is far more efficient than the channel. The channel process, for example, produces only about 1.8 pounds of black per 1000 cubic feet of gas, whereas the furnace process gives up to 7.5 pounds per 1000 cubic feet, or up to 3.6 pounds per gallon of liquid hydrocarbon feed.

NEW PROCESSES OF BASIC IMPORTANCE

In the past a number of processes have been developed which take a given starting material and then, by means of various chemical reagents, transform it into the final product, ultimately with the elimination of the reagents used to bring about this transformation. It is quite obvious that we are in the midst of a trend toward going directly from starting material to final product in one step wherever possible, thus eliminating both the expense of the intermediate chemicals and the cost of their processing. In particular, direct oxidation of a number of organic compounds is now being practiced with a significant cheapening of the product. This rather belated introduction of direct oxidation probably can be ascribed to two causes: In the first place, it often is easier and cheaper when operating on a small scale to proceed through chemical intermediates rather than by direct oxidation. In the second place, direct oxidation in many cases is so difficult to regulate and control that only recently have we found the means necessary to handle it successfully.

Table 1 shows a number of specific, recent applications of oxidation in the petrochemical industry. The first two cases, acetylene and hydrogen cyanide, have emerged only recently as commercial ventures, yet are already in the multimillion pound per year class. The conditions for the partial oxidation of natural gas to acetylene are, roughly: 1.5 volumes of natural gas and 1 volume of oxygen are preheated separately to about 950°F., mixed, reacted in a combustion chamber, and then rapidly quenched with water. The reaction temperature is 2700°F. and the contact time 0.001 to 0.01 second. The effluent gas contains about 8.5 per cent acetylene, representing a 30 per cent conversion of carbon in the methane to acetylene. The acetylene is recovered from the mixed products by selective absorption with solvents such as dimethyl formamide. In the hydrogen-cyanide process, air, methane, and am-

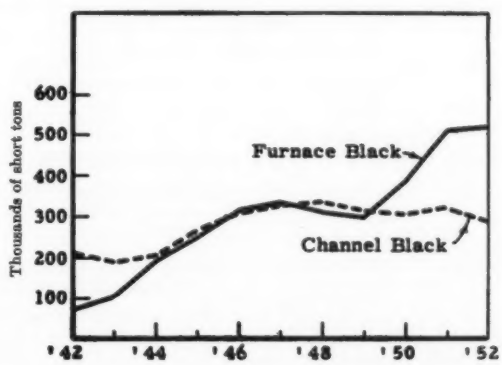


Figure 3. U. S. Production of Furnace Black and Channel Black

TABLE 1
Oxidation

Raw materials	*Products*
Methane	Acetylene
Methane and ammonia	Hydrogen cyanide
Propylene	Acrolein
Propane and butane	Methanol, formaldehyde, acetaldehyde, acetone
Butylenes	Maleic anhydride
o-Xylene	Phthalic anhydride
p-Xylene	Terephthalic acid
Cumene	Phenol and acetone
Propylene glycol	Pyruvic aldehyde

monia are reacted catalytically over platinum at about 1800°F. to produce hydrogen cyanide in a 75 per cent yield. Isolation of the hydrogen cyanide involves selective absorption and distillation.

Direct oxidation of lower saturated hydrocarbons has expanded rapidly in the postwar years. Table 2 shows a typical product distribution reported from the oxidation of butane, along with the principal uses for the products so obtained. One difficulty which this direct oxidation has faced in the past has been an overproduction of formaldehyde relative to other products. It is claimed that this now has been overcome and that, with butane oxidation, at least, the formaldehyde production is greatly reduced. Actually, little has been published on commercial operating conditions, although it is reported to be a catalytic oxidation carried out at somewhat elevated pressures.

Probably one of the most unique and interesting of the new oxidation processes is that for the production of phenol and acetone from cumene. Cumene (isopropylbenzene) is prepared by standard alkylation techniques from benzene and propylene. The process for cumene was developed and utilized extensively in World War II to augment our supplies of aviation gasoline. The basic reactions for the formation of phenol and acetone from cumene are:

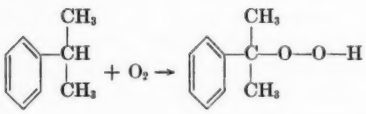
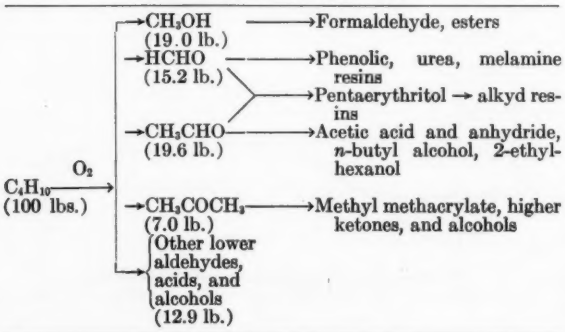
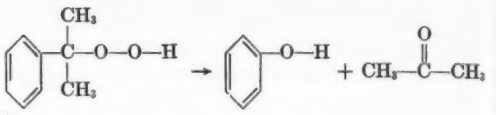


TABLE 2
Butane Oxidation Products





High-purity cumene is blown with air at 265°F. until about a 25 per cent conversion to cumene hydroperoxide is obtained. This material is then treated with dilute sulfuric acid, whereby the cumene hydroperoxide cleaves to phenol and acetone as shown. The oil phase containing the products in cumene is separated, the products are isolated by distillation, and the cumene is recycled. This type of reaction, the oxidation of a tertiary carbon atom, has considerable possibilities for other applications and is currently of interest in the production of cresols from methylcumenes. At present, several manufacturers are about to produce phenol by this cumene route. It is very likely that operating experience on a large scale will suggest some modification of the reaction conditions outlined above, and also lead to simplifications in recovering and purifying the product. In passing, it is interesting to note that three other phenol syntheses are still in active competition today, namely, the chlorobenzene route, the Raschig process, and the sulfonation route. Furthermore, additional phenol capacity by sulfonation is being built at the same time that the cumene process is about to come on stream, and in the same general geographical area.

TABLE 3
Chlorination

Raw materials	*Product*	*Major use*
Ethane-ethylene mixture	Ethyl chloride	Tetraethyl lead gasoline additive
Propylene	Allyl chloride	Glycerol
Butadiene	1,4- and 1,2-Dichlorobutene	Hexamethylenediamine for Nylon fiber
Pentanes, cyclopentadiene	Hexachlorocyclopentadiene	Chlordane, aldrin, dieldrin insecticides

Table 3 shows several chlorination reactions that have achieved commercial success recently, and also indicates the more important disposition of the reaction products. From the chemical standpoint, one of the most interesting of these is the manufacture of ethyl chloride from an ethane-ethylene stream by a combination of substitution and addition reactions. Ordinarily, ethyl chloride is made by the catalytic addition of HCl to the ethylene in a C_2 stream, the ethane being an inert diluent. In the case of this modified process the ethane-ethylene stream is first reacted with chlorine under such conditions that the ethane reacts in preference to the ethylene, thus leading to the formation of ethyl chloride plus HCl. In a second reaction zone the ethylene and the HCl are then combined to give more ethyl chloride. Suitable conditions for the first

step, that is, the preferential reaction of ethane and chlorine, call for a temperature of around 300°C., and a mole ratio of ethane to chlorine of about three to one. The second step, the reaction of HCl and ethylene, is done conventionally over a metal-salt catalyst. The remaining reactions shown have all achieved large-scale operation and appear to be gaining in importance with time.

The following are some important applications of the Oxo, or carbonylation reaction:

$$CH_2CH{=}CH_2 \xrightarrow{CO + H_2} CH_3CH_2CH_2CHO \xrightarrow{O_2} CH_3CH_2CH_2COOH \xrightarrow[Co]{} (CH_3)_2CHCHO$$

$$C_7H_{14} \xrightarrow[Co]{CO + H_2} C_7H_{15}CHO \xrightarrow{H_2} C_7H_{15}CH_2OH$$

$$CH{\equiv}CH \xrightarrow[Ni(CO)_4]{CO + CH_3OH} CH_2{=}CHCOOCH_3$$

This reaction has been adapted from German work which became known after the war. In one variant an unsaturated compound is reacted with carbon monoxide and hydrogen in the presence of a cobalt catalyst. The reaction is carried out under a pressure of 3000 pounds, at a temperature of 350°F., to give an aldehyde. The reaction mixture is freed of cobalt and the aldehyde is then recovered. As shown, the aldehyde from propylene is oxidized to butyric acid to be used in the manufacture of cellulose acetate butyrate, while that from C_7 olefinic gasoline cut is hydrogenated to give an isooctyl alcohol which is used in plasticizer manufacture. This last alcohol is very interesting in that it is in direct competition with the 2-ethylhexanol made from acetaldehyde through a series of aldol reactions. It remains to be seen whether both alcohols, or only one can survive economically. In another variant of this reaction the unsaturated compound is reacted with nickel carbonyl, carbon monoxide, and water or an alcohol. This leads to the production of an acid or an ester. This reaction is now the basis for the commercial manufacture of acrylate esters starting with acetylene as the unsaturated component. The conditions have been disclosed as reacting approximately equimolar ratios of acetylene and carbon monoxide with an excess of alcohol in the presence of HCl and nickel carbonyl. Atmospheric pressure and a temperature of about 40°C. are employed. The reaction rate is rapid, conversion is high, and the yield of acrylate ester is about 85 per cent. In the final product about 30 per cent is derived from the carbon monoxide contained in the nickel carbonyl, and 70 per cent from the added carbon monoxide.

The manufacture of aromatics from petroleum has assumed very large stature in recent years. Initially these aromatics—benzene, toluene, xylenes—were recovered from the streams in which they occur as the result of normal refinery processing. However, these sources proved inadequate to supply the demand, and as a result we see today that large quantities are made by the deliberate dehydrogenation of naphthene cuts. In this process both the C_5 and C_6 ring naphthenes are utilized. The C_5 naphthenes isomerize to C_6 rings and then dehydrogenate, the entire reaction being carried out over a single catalyst. As shown in Table 4 the result of this expansion is that today the petrochemical industry supplies more toluenes and xylenes than does the coal-tar industry, while looking to the future there seems little doubt that some day the same situation will prevail with respect to benzene. The remarkable success achieved in this field is a tribute to the skill of the industry in developing suitable catalysts and separation techniques to render possible this enormous production.

Ethyl alcohol, which for many years has been a large item in the petrochemical field, has also seen a significant new process introduced. Until recently synthetic ethanol was made by absorbing ethylene in concentrated sulfuric acid, hydrolyzing the esters thus secured, stripping the alcohol from acid liquors, and then reconcentrating the acid. The literature is replete with suggestions for carrying out this reaction catalytically, since the over-all reaction is simply the addition of a molecule of water to a molecule of ethylene, but no evidence of commercial success existed until the last few years. A direct vapor-phase hydration process is now in use. The operating conditions call for concentrated ethylene, a pressure of 1000 pounds, and a temperature around 300°C. Under these conditions the equilibrium conversion per pass is about 5 per cent when operating with a steam to ethylene mole ratio of 0.6 to 1.

TABLE 4
Major Cyclics Produced from Coal and Petroleum Sources, U. S., 1952, 1000 Gallons

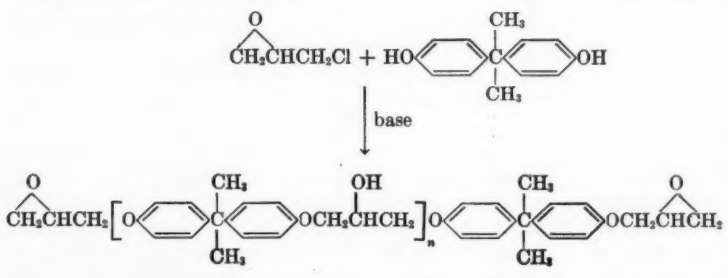
	Benzene	*Toluene*	*Xylenes*	*Total*
From tar crudes	216,149	41,257	10,173	267,579
	86%	39%	14%	62%
From petroleum	35,518	64,040	61,554	161,112
	14%	61%	86%	38%
Total	251,667	105,297	71,727	428,691

NEW PRODUCTS

In the foregoing we have noted a number of cases in which process considerations appear to be the predominant factor. Likewise, there are many cases in which the product factor appears to be dominant, for example, in the diversification of uses of certain raw materials and in the expansion of certain marketing areas. Acetylene in particular has found a number of new uses. Its conversion to acrylates by the use of nickel carbonyl has been mentioned as a newly established industrial operation. In addition to this reaction, the combination of acetylene and HCN to give acrylonitrile is now a major operation. Expansion in this chemical has been brought about largely by the demands for acrylonitrile for fibers. Originally acrylonitrile was secured through ethylene oxide and HCN but it now appears likely that the acetylene will be the preferred route in future expansions—again evidence of the desire to proceed as directly as possible from starting material to

final product. Still in the initial stages are a number of acetylene derivatives, largely derived from German work. These are such things as cycloöctatetraene and the condensation products of acetylene with carbonylic compounds. In this last category we have propargyl alcohol, butynediol, and its derivatives such as vinyl pyrrolidone. The polymer of vinyl pyrrolidone was proposed as a blood-plasma substitute by the Germans and is now finding some acceptance for that use in this country. It is reported that acetylene and toluene will form the basis for a new synthesis of methyl styrene, but so far commercial operation has not started. In the meantime, however, methyl styrene has appeared on the market, made by the dehydrogenation of ethyl toluene. In this case it is hoped that the methyl styrene will compete successfully with styrene on the basis of somewhat different properties and possibly a slightly lower price. The tremendous expansion of vinyl chloride resins also has occasioned a large increase in acetylene demand since much of the vinyl chloride monomer is produced from acetylene plus HCl. The vinyl ethers, derived from acetylene, are also growing, although slowly.

In the field of end uses there is no doubt that the tremendous demand for plastics has greatly influenced the petrochemical business. This, in fact, is one of its major outlets. The increase in this direction has been due in large measure to the greatly increased demand for what might be called the standard plastics, such as the phenolics, styrene, the vinyls, the acrylics, and polythene, while in addition to these standard items there have been very interesting developments in modifications of the existing polymers and copolymers, as well as in the development of newcomers. In this latter category some of the most interesting are the fluorinated materials, such as tetrafluoroethylene, chlorotrifluoroethylene, Terylene, or Dacron, and the new type of epoxide resin. These last resins which are known by various trade marks, such as EPON[2] resin, are essentially the condensation products of epichlorohydrin and polyhydroxy compounds. The following reaction shows the structure for such a material derived from epichlorohydrin and bisphenol:



These resins still contain the epoxy grouping and hence react with a wide variety of reagents. Reaction with drying-oil acids leads to varnishes with short drying times and outstanding alkali resistance. Condensation with polyamines leads to the formation of cross-linked structures without the evolution of any volatile material. In consequence, it is possible in this way to come to thick surface coatings in one application, to adhesives, and to casting and potting compositions. The structural modifications of this type of resin are obviously very great. At the present time the potentialities of these materials are just being uncovered and it appears likely that they will experience considerable growth in the future.

In a field somewhat related to the plastics we find a good deal of activity in the manufacture of polyhydroxy compounds. Synthetic glycerine made its appearance during the period we have under review. In addition to glycerol, several derivatives made by the condensation of formaldehyde with another aldehyde or ketone appear. Generally these have been made with the expectation that they would find a useful place in the alkyd resin field. Thus we find that pentaerythritol from formaldehyde and acetaldehyde has become a 50 million pound per year chemical, while similar derivatives from formaldehyde and propionaldehyde, butyraldehyde, and cyclohexanone have all been offered. In a sense the EPON resins mentioned above are also in this category.

While synthetic detergents have their origin considerably earlier than the period under review, nevertheless their growth has been very great in recent years. At present the most widely accepted material is the sulfonate derived from dodecylbenzene, which in turn is prepared from benzene and propylene tetramer. The syndets now represent a little over 50 per cent of the total soap market in the United States. The recent growth in the sale of liquid products is of considerable interest and may presage something of a change, since heretofore this has been a relatively small market.

In the agricultural field a number of materials have appeared which derive at least part of their raw materials again from the petrochemical field. These include such materials as DDT, benzene hexachloride, chlordane, aldrin, dieldrin, endrin, isodrin, and allethrin.

Besides the materials enumerated so far, we also have a group of miscellaneous chemicals which have been introduced to the trade and appear to be headed for success, although their ultimate volume is not clear. These include such materials as various alkylated pyridines, special solvents such as diisobutyl ketone, various amino compounds, and the like. Every year a large number of new materials is offered the trade by the petrochemical industry, and of these only a limited number survive to commercial fruition.

DEVELOPMENTS IN EQUIPMENT, TRANSPORTATION, AND STORAGE

In any discussion of recent advances in the petrochemical industry, due credit must be given to new de-

[2] Trademark registered U. S. Patent Office.

velopments in equipment and instruments, and to innovations in storage and transportation for the very important part they have played in promoting this technology. Electronic computors have made possible more refined calculations for plant design with attendant increase in performance and saving in capital. New control instruments have appeared constantly and have become irreplaceable equipment in many operations. It has now become commonplace to analyze gas streams continuously by such means as infrared spectra, paramagnetic properties, and ionization by beta rays. New equipment for liquid-liquid and vapor-liquid contacting has appeared, giving both improved efficiency and reduced capital. The gas turbine as a prime mover appears to be taking its place in new plant equipment, and very recently there has been activity in the use of expansion turbines for refrigeration.

From the economic standpoint, important advances have been made in the transportation and storage of raw materials and products. Seagoing tankers are now used for the movement of solvents, and ocean shipment, by barge, of anhydrous ammonia has been started. In another effort to reduce costs, natural gas is being stripped of its higher components just prior to delivery, and these materials are then used for chemical syntheses so as to have the site of manufacture near to consumption. The storage of propane and butane has long been a vexing problem because of the variation in seasonal demand for these materials. A very ingenious solution has been found by the washing out of an underground cavern in a thick salt formation. A number of these caverns are now in use for the storage of LPG, and plans have been made to extend this practice to the underground storage of ammonia.

FUTURE PROSPECTS

The petrochemical industry has been spending increasing amounts on research and development paralleling the increase in total U. S. industrial research and development effort. These expenditures imply confidence that the future of this industry is still extremely promising. In reviewing these activities of the past several years, one is led to the conclusion that the future will hold very definite advances so far as the understanding of reactions is concerned and the development of new catalysts and new ways of achieving desired end results. Further, it appears that certain selected areas will still have considerable growth, notably the plastics field and probably the agricultural field. Certain raw materials obviously will continue to have much work done on them, leading to further derivatives; acetylene appears to be a material definitely in this category. Finally, the increased cost of plants and the complexity of many of today's operations have focused ever increasing attention on means of reducing capital and operating expenditures so that it appears likely that a good deal of the research effort of the future will be channeled in these directions.

The factors which have led to the spectacular growth of the petrochemical industry are still operative and all forecasts agree that the future will see continued expansion for some time to come.

USE OF RADIOISOTOPES

A TWO-WEEK workshop on the Use of Radioisotopes in High-school Science Teaching will be held at Iowa State Teachers College, Ceder Falls, Iowa, June 13–25, 1955. It will be conducted under the direction of the science department of the college with the technical assistance of the Atomic Energy Commission. The local staff will be augmented by visiting scientists who are authorities in their field.

This is a pioneering attempt to meet the needs of high-school teachers and teachers of beginning college science courses by providing them firsthand acquaintance with radioisotopes. The workshop is planned with the idea that the use of radioisotopes for this purpose is both practical and safe. Lectures, audio-visual aids, and individual study will be used to present the subject. Participants will obtain direct experience with instruments and radioisotopes through laboratory work each day. Considerable attention will be given to the development of experiments suitable for use by each teacher in his or her teaching position.

Enrollment in the workshop is restricted to 24 participants in order that proper laboratory experience may be provided for each. A grant from the Standard Oil Foundation, Inc. has made possible the offering of 20 scholarships. Married teachers are invited to bring their wives. Housing for both will be provided in one of the men's dormitories.

Address your inquiries to J. W. Kercheval, Science Department, Iowa State Teachers College, Cedar Falls, Iowa.

THE NATURE OF SCIENCE AND THE TEACHING OF HIGH-SCHOOL CHEMISTRY[1]

GEORGE P. KLUBERTANZ, S.J.
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WHAT is proposed in this paper is not the addition of more material to courses, but an over-all point of view and a particular emphasis. Even in introductory courses the student needs to know what *sort* of knowledge science is, whether he will make a lifework of it, or whether he will go on to other kinds of activity.

It is a common—and often justified—complaint of graduate teachers of science that students, at the beginning of their graduate work, need to unlearn much of what they had previously learned. They can make no progress in research unless their thinking is not closed against new theories and techniques. Often, however, students resist this "open" attitude, even though they have been taught by very good chemists with great zeal for teaching and real devotion to students. How can future scientists acquire the basic concepts of chemistry without misinterpreting the truth-value and the permanence of these concepts?

Then there are the students taking basic chemistry courses who never continue on with the subject. As Conant (*1*) has made very clear, every citizen today needs to know something about science. He need not remember any particular formula, or any particular fact, law, or theory, but he must know what science is for many reasons. First, any human activity which has a large impact on humanity is a matter of concern to every citizen in a democracy. Second, the citizen can react to science in various ways. He may be suspicious and wish to restrict the teaching and even the research activities of scientists. Or, amazed by the successes of science in one or more fields, he may be willing to abdicate his rights and responsibilities as a free citizen to a superior group. Or, observing the changes in scientific theory, he may conclude that all knowledge is subject to the same variations; that there is no lasting truth anywhere; and that consequently there are no fixed points of reference in terms of which he can orient his life. Such attitudes automatically generate insecurity and may easily lead to psychological problems, or to an abandonment of all personal responsibility. Lack of understanding of the nature of scientific knowledge is at the root of these reactions.

THE KINDS OF KNOWLEDGE

The analysis of the nature of science cannot legitimately be made apart from a clear and careful inquiry into the whole scope of human knowledge. At the very least, it is necessary to set down these well established conclusions:

(1) There are many intrinsically different kinds of knowledge.

(2) Intellectual knowledge is most basically divided, according to the way in which it takes place, into spontaneous, humanistic, and scientific knowledge.

(3) Scientific knowledge is further divided, according to its proper subject matter, into the various scientific disciplines, such as geology, astronomy, mathematics, and chemistry.

(4) Scientific knowledge in general is characterized by (*a*) organization and unity, (*b*) principles that are directly and necessarily connected with its subject matter, (*c*) explicit and conscious concern with proof, demonstration, and verification, and (*d*) subject matter which is proper to it, in the sense that no other knowledge deals with precisely the same considerations about that subject (*2*, *3*).

THE ELEMENTS OF NATURAL SCIENCE

In some sense, *technique* or skill pertains to science, yet technique and science are not identical. A scientist knows *why* a certain procedure must be followed as well as what the procedure is. He knows how to set up a problem and to ask the kind of question that can be answered. This is much more than mere skill or technique. Technique pertains to science, not because technique is a part of knowledge or some form of knowledge, but because of the nature of the method used in science to gain evidence and proof (*i. e.*, the experimental method) and because of the object of science (*i. e.*, knowledge about natural things through experiment or controlled observation).

As well as technique, a consciously developed *method* (*4*) belongs to science. In science one cannot bank on "lucky" events. Moreover, method in science is both a method of *discovery* and a method of *reasoning* and *verification*. As far as the method of discovery is concerned, it is, in general, "observation of facts" (disregarding, for the moment, the ambiguity of the term *fact*). This statement, however, is not nearly enough. Any scientific knowledge has as its starting point a careful and detailed observation of the data that are pertinent. Hence, we must sharpen the notion of *observation*. The kind of observation most proper to science is that of experimentation. A straightforward and rather passive observation of nature is found in some sciences where nothing else is possible (*e. g.*, astronomy, astrophysics), but as far as science can manage the situation such observation is rather to be avoided. It is time-consuming and haphazard; it is normally mixed with so many and

[1] From a lecture delivered on July 7, 1954, at the Institute for the Teaching of Chemistry, St. Louis University.

such complicated irrelevancies as to frustrate investigation. Hence, science has developed the method of experimentation. Basically, experimentation does not wait for nature to show itself, but puts the natural object in such a condition—asks a question, as it were—that it must act, or else show its nature in not acting. Moreover, the more highly developed the experimental technique, the more precise and also the more selective its results. This is all to the advantage of the scientist, since it tends to exclude all the evidence that is not immediately pertinent to his question. It is because of this method that technique or skill is necessary for a scientist.

As far as the method of *proof* is concerned, we shall have to distinguish proofs of fact, of laws, and of theories. Proofs of fact have a peculiar position in science; for it is not so much the occurrence of a single event that is to be proved, but rather of the event as instance of a type, and of this kind of fact the easiest sort of proof is another event of the same type. Hence, though science is based on facts, it is not historical knowledge or existential knowledge. We shall see this aspect of the scientific fact more fully a little later.

The proof of a general law can only be the inductive reasoning and generalization that led to its original formulation, or some repetition of that reasoning.

The "proof" of a theory as pure theory lies in the verified consequences. In strict logic, to establish the consequent is not to establish the antecedent. Yet a scientific theory is commonly held to be proved in this way, and so we must conclude that the word "proof" has acquired a special meaning which can be understood only after we understand what scientific theory is and how it functions.

THE OBJECT OF SCIENCE: THE OBSERVED FACT

We must now return to the *fact*. Many people seem to think that a fact in science is the simple, total reality of a thing or an event as it actually occurs. Scientists realize that this is not the case. Experience as such is both too rich and too poor; too rich, for it always contains a multitude of sheer contingencies and irrelevancies; too poor, for as it comes to us without interpretation it often is no more than a brute signal that something is going on.

In virtue of the scientific method itself, the scientific fact undergoes a first limitation: A fact is the result of the special method of science; it is the result of an experiment, or at least of a controlled and selective observation. Second, the scientific fact is often adjusted by virtue of a general principle. We teach our students that there is always some error in our observations. To permit the student to think that the *corrected* observation is a simple, direct, unqualified evidence may leave him at peace but it will not teach him to think as a scientist. Third, the scientific fact is very often interpreted evidence. For example, we often say that we "see" the track of an electron in a cloud chamber. We see a disturbance occurring and leaving a track; we argue—at least partly on a theoretical basis—that this activity was caused by the passage of an electron; we combine the observation with the reasoned conclusion into one single statement, "We see ...." Note that I am not saying that the conclusion is false; I am trying to point out the complexity of what is often called a fact.

LAWS IN SCIENCE

The mere accumulation of facts is not yet science, except to the extent that the very data may be shown to be consequences of already constructed theories, or may be expressed in theoretical terms. The first truly scientific stage of science consists in formation of *general laws* from observations. Generalization in science may in rare cases be immediate, especially in psychology and biology. More often, however, generalization cannot be immediate, since there is no total and absolute uniformity of experimental data. In some cases (mentioned above) there may be error in the details of the observation. In other instances the objects themselves may not be totally consistent. An instructive case is that of Boyle's law of gases. The first experiments were conducted with relatively crude apparatus and—as we now know—within a very limited range of variability. Under these conditions a uniformity was observed. With present-day apparatus the total range of results seems to yield no simple uniformity at all. In conditions where uniformity does not immediately reveal itself, statistical methods can be used to build generalizations.

In these general laws we can find the essential traits of one kind of scientific knowledge. Already we have a proper subject: the facts as selected and interpreted by the very experiments that bring them forth; a proper method: experiment; proper principles: the validity of experimentation and the legitimacy of generalization, both immediate and statistical; and proper methods of proof: the repetition of experiments under controlled conditions and the *prediction* of results under similar conditions. A great deal of science could be handled at this level of development alone.

THEORIES IN SCIENCE

Modern science has developed further and in a different direction. As long as there were but few general laws it seemed easy to keep them in mind, and to use and apply them. However, the method of experiment and generalization as such gave no insight except *that* this and so is what happens. Observation of freely falling bodies, for example, was able to yield very exact laws. Scientists were dissatisfied with these laws for two reasons.

The first inadequacy of a simple descriptive law is that it does not tell *why* something happens. (Note that in the mode of spontaneous knowledge, and in all ontological knowledges, "why?" is a question about an ontological cause. In more complicated situations we often cannot determine the cause directly; then "why?" asks about the cause in the sense of "necessary antecedent." In still more complex situations, where

we can no longer determine even the ontological antecedents clearly and distinctly in themselves, "why?" means, "How can we consider this so as to make it intelligible?" In this third sense, "cause" is indistinguishable from "logical reason.") Again considering the law of freely falling bodies—such a descriptive law does not say "why" bodies fall, and no increase of generalization or of experimentation will yield such an understanding.

The second inadequacy of a simple quantitative law is that it gives no ground for correlating the measured activity with other behavior of bodies. In other words, such a law cannot serve as an organizational principle of knowledge. Moreover, such organizing or unifying principles cannot be derived from experiments either directly or by generalization.

We can also illustrate the same situation with an example closer to chemistry. Almost from the beginning of recorded knowledge people knew something about combinations of material substances. Continued investigation produced a great many laws, both qualitative and quantitative, which were accurately known, established, and verified. But these descriptive laws did not show why combinations occurred the way they did.

In both cases scientists began to construct theories. In the case of falling bodies, the theory of "proper place" was invented. The universe was considered to center around the earth, and the center was the proper place for earthy matter. Water was "at home" above the earth; air, above the water; fire, above the air. This theory gave an intelligible spatial picture, and an easily understood reason for falling bodies—they were merely seeking their proper place. In addition, the theory enabled scientists to correlate other observed behavior; rising bodies, like fire, were also "homing." On the added supposition of circular motion around a properly disposed set of eccentric axes, the theory accounted for the motions of sun, moon, and stars. Note the nature of scientific theory. It does not arise from facts distinct from those which give rise to the laws. The process is not one of generalization, even though a theory always is very general and inclusive. Nor is the theory induced from the facts or the laws. It is constructed and imposed on the laws and facts. First of all, a theory is the product of a creative imagination; someone had to imagine the universe in a geocentric pattern, and endow the enclosed space with inherent characteristics—that of being "home" for a certain kind of body. This image or model was then employed to unify the various facts and laws already known about the location and movements of bodies. The theory had to be internally consistent; for example, the natural presence of earthy matter away from the center could not be allowed. Without consistency a theory cannot even be conceived as a possible explanation. In addition to internal consistency, three relations are necessary.

(1) The theory must take account of all the relevant data and laws.

(2) Its relation to experience and/or experiment has to be able to be clearly pointed out (the "epistemic relation" of Margenau (*5*)).

(3) It has to be fruitful, in the sense that it can suggest new observations and experiments, and predict results.

The theory of proper place filled these conditions for a long time. Gradually new data were discovered which became more difficult to fit in with the theory. Supplementary theoretical hypotheses had to be invented (for example, the epicycles) until the theory became very cumbersome. Finally, after a few scientists of rare imagination had suggested an alternative, the heliocentric picture of the universe was accepted.

However, no single theory could immediately replace the geocentric one, and it was not until Kepler's laws of planetary motion and Galileo's laws of falling bodies were unified in the single theory of universal gravitation and motion constructed by Newton that the heliocentric theory won unquestioned acceptance. By and large, the theory of universal gravitation exists as a scientific theory on the basis of the same kind of argumentation and proof as that which the geocentric theory had in its favor.

Take a second case, that of combinations of relatively simple substances. The first theoretical unification was achieved by the phlogiston theory which was widely held for many years. It was ultimately replaced by the operational notion of element developed by Lavoisier, and the atomic theory with its numerous modifications and developments. The phlogiston theory was abandoned when many refractory facts refused to fit in with the theoretical account, and after a new approach was offered which could include all the hitherto unmanageable data. The atomic theory and the notion of element have been changed under the pressure of new data. (Of course, new methods of observation and new instruments have brought the notion of a certain discontinuity in nature into close relation with generalized observation and law.)

Out of these two cases we can derive a notion of the nature and function of a scientific theory. A scientific theory is a rational explanation of observed fact, such that, if the theory be granted, the data follow by way of logically necessary implication (*6*). This explanation may be a model which is drawn from other areas (of experience or reason), an abstract symbol, an operational definition, or a real trait selected as a clue to other characteristics. These "explanatory" factors are considered by the mind to be the originating source of the observed behavior, experimental results, classifiable similarities, etc. The purpose of such a constructed factor is to provide an intelligible explanation, to unify large masses of data, and to stimulate and predict.

TRUTH AND CHANGE IN SCIENCE

Method and technique, fact, law, and theory are the essential elements in modern science. Each one of them has to be correctly understood and carefully distinguished if students are to obtain an authentic understanding of science.

The general scientific *method*, as the basic method of careful investigation and critically judged reasoning, does not change, for it is characteristic of all scientific knowledge as such. This general method may be applied to problems to which it has never before been applied, and so a new scientific knowledge may be generated. But otherwise there is no change. Special scientific methodologies and techniques (skills) may well change, and if they are taught as unchanging a great harm is done to the mind of a student. Method, technique, and skill are neither true nor false in the strict sense of those terms; they are only successful or not. We should even be very careful in talking about the *right* way to perform an experiment. Within certain limits, of course, we can call techniques right or wrong. But we should, as teachers, distinguish inventive curiosity from slovenliness, and not let the practical necessities of order be turned into theoretical rigidity.

Facts, provided that they are perceived without error and are uncomplicated by theoretical additions, do not change. The facts may not have been the facts that the original investigators thought they were; the early phlogistonists thought the products of combustion weighed less than the unburnt materials. The facts may have been colored by interpretation; Lamarckian biologists spoke of the "stretching" of the giraffe's neck as a fact. The selective limitations of experiment and of instruments may not have been sufficiently realized; some years ago many physicists thought they had evidence that atoms could not be broken up. Moreover, the meaning of the facts may change, as the context of larger (theoretical) ideas in which they are found changes. For example, "all heavy bodies fall down" is a generalization from facts, but the meaning of "down" is different as the earth is considered flat or round; likewise, the meaning of "heavy" has changed with the introduction of the concept of relative density. If, on the contrary, the facts are truly such as reported, and are presented as simple evidences, then they do not change unless the natural object itself changes (and this kind of change is not relevant to our present discussion). Under these same conditions of freedom from error and from theoretical interpolations, the facts may be said to be true and certain.

Laws which are properly established cannot change unless the facts on which they have been based change. But the generalization may be discovered to have been illegitimate (as in the case of Boyle's law) by excess; later scientists may find out that they must limit the application of a law. This merely means that scientific laws are capable of increased accuracy and precision and can have a greater or lesser application. We may discover, for example, that metals under conditions of extreme cold behave in different ways; this does not change what we say about their behavior at 70°, though we now know we must add this qualification. Laws or generalizations are simply true and certain when they are immediate and are expressed with all relevant qualifications. Mediate and indirect generalizations are not simply and literally true; they are true only in the statistical sense according to which the generalization was first made. "*X* always does this, "as a statistical universal, means "*X* always does such a kind of action whose limits of variability are these, and the likelihood that it will do precisely this or that is expressed as its probability." Moreover, we must be careful that the generalizations have neither too wide nor too narrow an extension. Too often we say "all" when we mean "all within the range x to z." However, such a limitation is often not discoverable at the time of the first generalization, and so we must keep an open mind about the possibility of future modifications of even the most cherished scientific laws.

Scientific *theories* most obviously change, and by their nature probably will continue to change when they become cumbersome or relatively useless. The "truth" of a scientific theory is harder to state. Ordinarily, we say that a statement is true when it expresses what is, or denies what is not; it is false when it expresses what is not or denies what is. A scientific theory is not a simple statement of fact. Take for example the "tunnel effect" in atomic theory. Does anyone mean that there really is within the atom a hill or barrier through which there are holes like tiny tunnels? Does any scientist think that electrons are little wheels spinning clockwise or counterclockwise? Are there hoops or ropes that bind atoms together? The questions are now considered preposterous, but let us not too easily ignore the implications of their obvious answers. We defined a theory as a rational construct imposed upon data to explain them. Because constructs differ, the relation of theory to reality is variable. For example, the planetary structure of the solar system began as a theory; it can be called a "univocal" theory, in the sense that it was explaining the movements of solid bodies by a picture of solid bodies, and so forth. At the other extreme, some of quantum mechanics may be called purely symbolic; the formulas work, but we cannot express clearly and certainly what each formula symbolizes (*7*). Between these two extremes there are theories which work, and which have a partly literal, partly symbolic value. From this point of view, the atomic theory will serve as a mixed example. As a statement of some kind of relative discontinuity in nature, that "nature somehow comes in packages" (particles, quanta of energy, and so forth), the atomic theory is a straightforward generalization. But that these "packages" are spatially distinct little bodies within the atom; that atoms and molecules are mere aggregates bound together with bonds—electronic, magnetic, or otherwise; that all change is accidental change of substantially unchanging identical components—these parts of the atomic theory are strictly constructural.

Consequently, "theory" in science does not always have one and only one relation to reality (*8*). Most scientific theories would have to be divided into purely constructural, hypothetical, and descriptive elements for an accurate epistemological evaluation. We should

therefore most correctly speak of a scientific theory as "good" or "successful" rather than "true." If we must speak of the "truth" of a theory, we must change the meaning of the term *true*, so that it means "helpful in understanding, related to the facts, internally coherent, inclusive of all the pertinent facts and laws, coherent with related theories, fruitful of new experiments, and verified by fulfilled predictions."

APPLICATIONS TO TEACHING

Students who grasp these distinctions, and who have, even at the introductory level, the beginning of an understanding of law and theory, will profit a great deal. Future scientists will remain open-minded and creative if they realize the nature of the generalizations and theories they have learned. Yet there is also a core of fact and law that they can reasonably be required to learn and even memorize. We can train them in carefulness in experiment, in accuracy and objectivity in reporting, without closing their minds. Future nonscientists also can acquire a basic understanding and respect for science. On the one hand, they will not fear or hate science on the false ground that it might destroy their way of life. On the other, they will not acquire the "Sunday-supplement" mentality, mistaking theory for literal fact, or translating it into univocal practice, or relinquishing the conduct of their lives (civic or personal) into the hand of a scientific elite and expecting to be cared for in return.

Moreover, it is not too hard to do this. When a teacher is explaining an experiment, the nature of experiment in general can be brought out. Instead of saying, "The *right* way," the teacher can say, "So far, the most successful way to find this out is. . . ." Instead of implying that an experiment reveals simply and directly the entire discoverable truth about a thing, the teacher can explicitly point out that the experiment is designed to answer a very definite, limited question, but that there are other aspects of the thing which are necessarily ignored. When a law is being taught, the nature of scientific generalization can easily be pointed out, especially since the students are usually required to conduct an experiment whose actual results will be somewhat different from exact results of the textbook. In a statistical generalization the teacher can point out that the average is not necessarily ever attained in experiment, and explain why a precise quantity is set down. When students are taught to compute the probable error, it will take only a few moments longer to explain how error creeps in, how it is recognized, and how it is corrected. It will be very helpful if the student is introduced to a particular theory by way of the evidence which has to be considered and the problems that arise. For example, when a teacher comes to the theory of the atomic constitution of matter, he can summarize the evidence briefly, and then ask the pertinent question, "What can we do to unify and understand these facts and laws?" He can show the insufficiency of direct experience. Instead of saying, "The *answer* is that matter, though it seems to be solid, *really* is mostly empty space . . . ." He can say, "Let us suppose that matter is something like . . . ." The first of these two ways is not scientific at all, and does not produce scientific understanding. At best, it will be held in rigid, uncomprehending memory; it may lead to misunderstandings. True, the second way may take a little longer the first time. In the long run it may well save time, for brute memory is slow and hard. Moreover, future explanations can be much briefer. Even if to explain a theory as a construct may take longer, the difference to the student is worth the time it takes. Since our students live in an age of science, and since we hope that at least some of them will contribute to its advancement, it is surely a matter of intense concern to us that they have a proper and balanced appreciation.

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ERRATUM

On page 72 of the February, 1955, issue of this Journal ("Studies of Egyptian Bronzes," by Herbert Weisz) is the statement: "*Zinc* was found in the sectors of Ring III; the reagent was morin." This should be: "*Tin* was found. . . ."

ATHANASIUS KIRCHER, S.J.

A Contemporary of the "Sceptical Chymist"

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THE birth of modern chemistry was a slow process and, though we give Robert Boyle the title of "father of modern chemistry," yet we do not claim that from the time he wrote his book "The Sceptical Chymist," science cast off its shackles of ignorance and superstition and began an unbroken course of development. Boyle's "fatherhood" was less a personal generation than a stimulus to others to bring to birth a new science. He pulled down and undermined old, unproductive ideas and theories, leaving space for the erection of the new. His "Sceptical Chymist" is, as its title claims, the treatise of a sceptic, pointing out the fallacies in the accepted doctrine, asking "why?" where others preferred to accept without question. It is the negative side of the book, not its positive, and, indeed, often unsound side that won for Boyle his title and set the chemists on the slow, erratic road to modern science.

In the year 1661 when Boyle wrote the book, there were many who practiced the art of "chymistry." There was no lack of experimenters, and experiments touched on all aspects of the subject in question. The experimenters were often men of brilliance, whose studies in other fields are still remarkable. But the chemistry of Boyle's day was based on false premises. What had been built so high could not be built any higher because the foundations were weak. Vague theories, insufficiently tried by experiment, were the basis of chemistry. In a fuddle of Aristotle's principles and qualities, which had been further complicated by the ignorance, and even by the willful obscurities of the alchemists, chemists of the day struggled along. They boiled, distilled, precipitated in experiment after experiment, but since the very fundamentals of their knowledge were incorrect, what real progress could they make? The practical arts of pottery and metallurgy could be advanced by purely empirical methods, but there was little hope of headway for the theorists, whose respect for tradition forbad them to question the wisdom of the ancients. This uncritical acceptance of the traditional notions was what Boyle had to combat. In freeing men's minds from these errors he permitted modern chemistry to come to birth.

It was such a situation that Boyle had in mind when he wrote in the preface of his book (*1*):

> I observe that of late Chymistry begins, as indeed it deserves, to be cultivated by learned men who before despised it; and to be pretended to by many who never cultivated it, that they may not be thought ignorant of it: whence it comes to pass that divers chymical notions about matters philosophical are taken for granted and employed and so adopted by very eminent writers, both naturalists and physicians.

Not only did Boyle condemn this acceptance without criticism of the traditional doctrine, but he also condemned the willful obscurities of many "chymical writers" with their "obscure, ambiguous, and almost aenigmatical way of expressing what they intend to teach that they have no mind to be understood at all" (*1*). He ridicules their teaching that *ubi palam locuti sumus, ibi nihil diximus*—"where we have spoken clearly, there we have said nothing at all!"

Boyle was not the only "sceptical chymist" of his day, and the purpose of this article is to introduce a little known contemporary of the "father of modern chemistry" who had a similar critical approach to the science. This other was not as brilliant a man as was Boyle, though his learning was vast. He was a sceptic, though by no means as sceptical as was Boyle, and often he fell into those errors which Boyle warned others to avoid. Nevertheless, this man, the Jesuit Athanasius Kircher, deserves recognition for his work, small though its importance may have been, which contributed to the birth of modern science.

KIRCHER'S GENIUS

Athanasius Kircher was born on the second of May, 1601, in the little town of Geysa, near Fulda, in Germany. In his boyhood he showed no very obvious signs of the genius that was to mark his adult life, and it was only with difficulty that he gained admittance to the Jesuit novitiate at Paderborn in 1618.

Kircher completed his elementary studies in the Society of Jesus in Germany, and then, when driven from his fatherland by the Thirty Years War, he was called to Rome. There he was to take the chair of natural philosophy in the Roman College. He arrived in the city in the beginning of 1634, the year after the second trial and condemnation of Galileo. From then until his death, in 1680, he had his headquarters in Rome, where he studied, lectured, experimented, and wrote on the vast and general topics of the science of his day.

Kircher had arrived in Rome well equipped for his work. His languages included almost all the modern European tongues as well as the ancient languages of Latin, Greek, Hebrew, Syriac, and Coptic. He was a

skilled experimenter and already had a book on magnetism to his credit, as well as another on Egyptian hieroglyphics. Moreover, he had interested himself in astronomy, a very topical subject just then. As early as 1625 he had observed sunspots through a primitive telescope and, in commenting on this astounding fact, had come to the revolutionary conclusion that the sun was made of the same materials as was our earth, and not of the unchanging quintessence of the ancients (*2*).

By the time he was 40 Kircher had studied and written on many other subjects. Several books on the ancient Egyptian obelisks, which had about that time been resurrected from the ruins of old Rome, appeared in those years. A mighty tome on music, "Musurgia Universalis," also belongs to this period, as do other writings on light, magnetism, certain mechanical devices, and even on ancient languages. Before his death Kircher had written more than 40 great tomes on scientific topics as well as a great number of smaller works and letters on similar matters.

This "universal genius," as he came to be known by his admirers, was a 40-year-old professor at the Roman College when the 12-year-old Robert Boyle visited the city, in 1641, in the company of his brother and their tutor. Boyle did not meet the Jesuit, nor did he visit the museum of natural history which Kircher was building up at the time. This was one of the first science museums in the world, and it lasted until the end of the last century when its contents were divided among the other museums of Rome. Later Boyle regretted very much that he had missed this chance of seeing the very ingenious water-organs and other musical instruments which had been invented by Kircher and were to be seen in the "Museo Kircheanum" (*3*).

On the outbreak of rebellion in Ireland, which caused serious financial embarrassment to his father the Earl of Cork, young Boyle was forced to retire, first to Geneva and then to England. He never again came to Italy. Thus, all further chances of meeting Kircher were lost (*4*).

Kircher continued to write and investigate while Boyle was beginning his scientific studies in England. Many of the Jesuit's books were published in Amsterdam, whence there was frequent traffic with England, and from the references in Boyle's books we can see that he obtained and read many of these works.

The minutes of a letter from Boyle to another Jesuit, Gaspar Schott, have been preserved. Schott was at the time professor of physics at Augsburg in Germany, and had been one of Kircher's friends and assistants. In the letter Boyle thanks the Jesuit for the present of a book and grants him permission to incorporate one of his own books into a treatise Schott intended to publish in the future. When Schott's treatise appeared some years later, Boyle's "Newmatical Book" appeared, along with one of Kircher's works, in the same volume. Thus was another link forged between Boyle and the Jesuit scientist at Rome (*5*).

A letter from Sir Robert Southwell, dated Rome, March 30, 1661, shows that Boyle had not lost interest in Kircher, but had sent him several inquiries through their mutual friend Southwell. "Father Kircher," writes Southwell," is my particular friend and I visit him and his gallery frequently...all the questions you bid me ask him he affirmed to me in the same manner as you will find them written...," (*6*). Kircher's "gallery" was his museum of natural history.

Southwell comments on Kircher's credulous nature, "apt to put in print any strange, if plausible, story that is brought to him," and without doubt, credulity is a feature of several of Kircher's books. Many of them were vast compendia of stories, descriptions, and observations, some of which must have made Boyle smile, as they did Southwell. Yet Boyle was acute enough to see the truth and the value of much of what Kircher wrote. Never once does he descend to abusing the Jesuit's uncritical approach to his subject. He never refers to Kircher but as "diligent," "learned," "inquisitive," "industrious," though he may sometimes disagree with his findings. Kircher himself did much to make amends for his too trusting acceptance of stories in several of his later books which even approach Boyle's standard in their criticism of traditional theories. However, as will be shown, he could never claim to rank as a sceptic beside Boyle, and at times would even fall under the general criticisms which Boyle made of the chemists of his day.

When, then, in 1661 Boyle published his epoch-making "Sceptical Chymist" he could have had Kircher in mind among the learned men, who had begun to "cultivate chymistry...the very eminent writers, both naturalists and physicians" who were taking so many notions about chemistry for granted. However, Kircher was certainly not one of those "chymists" who sought to hide their meaning under "an obscure, ambiguous, and almost aenigmatical way of expressing what they intended to teach." Willful obscurity was not one of Kircher's faults. Kircher, though, would appear to come under condemnation for "relating experiments by way of prescriptions, not of relations, for building up on experiments he himself had never tried, and of doing injustice to his own good name" by countenancing others' vague, unsatisfactory teachings (*1*).

It was possibly out of respect for such men as Kircher that Boyle, always a courteous and generous adversary, refrained from mentioning by name the writers he had in mind when he made such criticisms.

Boyle's book was soon translated into Latin, the international scientific language of the day, and it is likely that it came into Kircher's hand before long. Without difficulty the Jesuit would have been able to read between the lines and see there the criticisms of his own credulity. However, he was not inclined to abandon the traditional doctrine that salt, sulfur, and mercury were the true principles of things. It was on this doctrine that Boyle had made his major attack, though he affirmed that if the alchemists, or the "spagyrists" as he called them, would only prove their theories by sound experiments, he would be the first to return to their opinions. Boyle wrote:

I have endeavoured to deliver matters of fact so faithfully that I may as well assist the less skilful readers to examine the chymical hypothesis, as provoke the spagyrical writers to illustrate it; which if they do, and that either the chymical opinion or the peripatetic, or any other theory of the elements differing from that I am most inclined to, shall be intelligibly explicated and duly proven to me; what I have hitherto discoursed will not hinder it from making a proselyte of a person that loves fluctuation of judgement little enough to be willing to be eased from it by anything but error.

Boyle was not wedded to his own opinion; he held his mind open for the truth.

"MUNDUS SUBTERRANEUS"

Kircher may have been answering this challenge when, in 1665, he published his most famous treatise, "Mundus Subterraneus." This vast work of 12 "books" in two separate volumes, was written in Latin. In it Kircher treats of everything that is to be found under the earth: of volcanoes, underground rivers and lakes, metals and metallurgy, underground animals and plants, and even underground men. The eleventh book treats of alchemy, a subject connected with the metals and minerals of the earth. Much of the treatise smacks of the over-credulous, but it is in keeping with the spirit of the times, and even Boyle would have passed over these doubtful matters and concentrated on what was of real value. Indeed, it is not hard to find rather similar descriptions of monsters and other incredible creatures in some of Boyle's works.

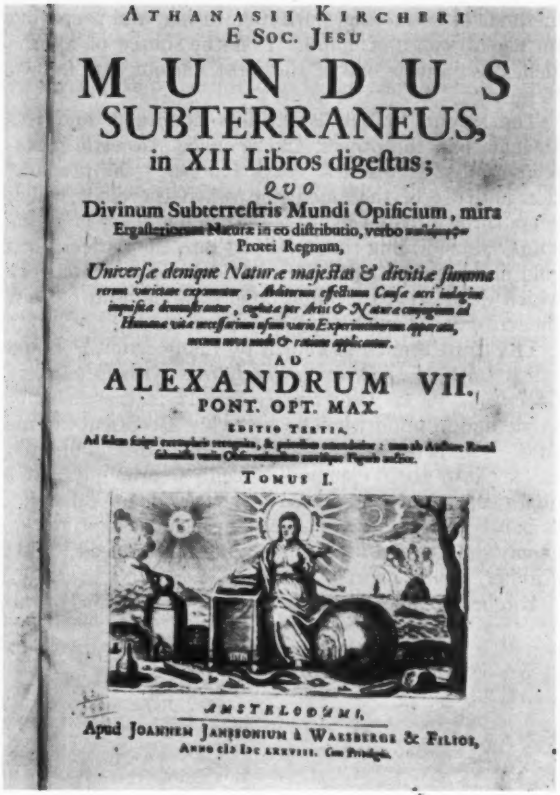
It is interesting to note that in the very year of its publication extracts from "Mundus Subterraneus" were published in the *Philosophical Transactions of the Royal Society* (7). Moreover, in the same year there is mention of the reservation for Boyle of a copy of the book at a London bookshop (8).

The book on alchemy carried the elaborate title of "Chymiotechnicus in Which All the Apparatus and Arts of the Chymical World are Described, Chymiotechnical Methods are Related to the Architype of Nature, and the Foundations of Pseudo-chemistry are Exploded" (9). The contents of this book must have interested Boyle intensely. In many particulars the work differs from Boyle's "Sceptical Chymist," though the general aim of the two books is the same. Kircher wrote:

My intention has been to separate truth from falsehood, the licit from the illicit, the honest from the fraudulent . . . so that learned men, both physicians and philosophers, when they have examined these matters and experiments, may, along with me, be able to discern truth from falsehood (9).

Kircher's book undoubtedly contains many errors, and at times verges more than a little on the over-traditional approach to the subject. Yet, like Boyle's book, this work marks the end of a period—the period of superstition and obscurity in chemistry, though there is as yet but the faintest glimmer of the dawn of the new, fertile, critical period of the science.

We may neglect most of "Mundus Subterraneus" as not pertinent to our inquiry, and concentrate on the eleventh book, "De Alchemia." This is divided into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E SOC. JESU

MUNDUS SUBTERRANEUS,

in XII Libros digestus;

QUO

Divinum Subterrestris Mundi Opificium, mira Ergasteriorum Naturæ in eo distributio, verbo [illegible] Protei Regnum,

Universæ denique Naturæ majestas & divitiæ summa rerum varietate expromitur, Abditarum effectuum Causæ acri indagine inquisitæ demonstrantur, cognitæ per Artis & Naturæ conjugium ad Humanæ vitæ necessarium usum variis Experimentorum apparatibus promotæ modis & rationibus applicantur.

AD

ALEXANDRUM VII.

PONT. OPT. MAX.

EDITIO TERTIA.

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TOMUS I.

AMSTELODAMI,

Apud JOANNEM JANSSONIUM à WAESBERGE & FILIOS,

ANNO cIↃ IↃC LXXVIII. Cum Privilegio.

Title Page of "Mundus Subterraneus"

two main parts; the first deals with alchemy in general, "De origine alchemiae" and the second is a critical study, leading to a rejection of the doctrine of the philosophers' stone, "De Lapide Philosophorum."

Kircher begins his investigation of alchemy by remarking that for many years he had been seeking information on this art. He questioned learned men in many lands; he read the books of Lully, Villanova, Roger Bacon, Paracelsus, Basil Valentinus, and many other famous alchemists, but nowhere had he found what he sought. Finally, he had gone to the very sources of alchemy, to the Hebrew, Arabic, and Egyptian writings of Zohara, Zadith, Hermes, King Haled, and many others, and in the end of all this search he was forced to complain, like Boyle, of the obscurity and the enigmatical expressions of these men. Indeed, he says, "I came to the conclusion that nothing was easier than to write in such a way, putting down the first things that occurred to them, the most ridiculous phantasies of the human mind, in twisted words, solely to confuse whosoever tried to read them" (9).

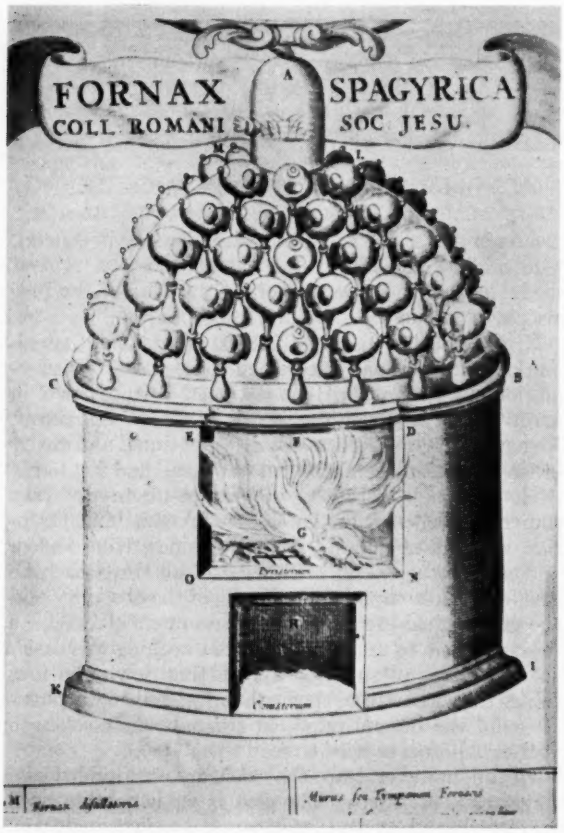
He did, however, learn that alchemy was divided into three main divisions. The first is an honorable, well developed, and ancient science, *Alchemia metallurgia*, the science of metallurgy, which is also known as *Chymia*. This branch of alchemy deals with the

methods of extracting, purifying, fusing, and preparing for use all types of metal. It is the source of all the alchemies, and is one of the most ancient arts known to men.

The second branch is far less honorable and less ancient than the others, and is called *Alchemia transmutatoria*. "It teaches," says Kircher, "the preparation and use of that medicine called the elixir which when thrown over a metal is said to perfect it in an instant, transforming the imperfect into the perfect, into gold and silver" (*10*). This is the branch of alchemy which deals with the philosophers' stone, and of that the writer will have more to say later on.

The third branch is known by many names. Some call it *Chymia spagyrica* or *analytica*. Others name it *Chemistria* or *Chymia medicinia*. It is the alchemy Boyle had in mind when he wrote his "Sceptical Chymist." This is the art of separating minerals and organic matter into their elements, essences, principles, and qualities, and applying these to the treatment of disease. It is a type of *materia medica* or pharmacology, an alchemy applied to medicine. This is indeed, adds Kircher, a praiseworthy study.

Kircher prefaces his more detailed descriptions of the techniques and instruments of the alchemists with words in keeping with what Boyle required of chemical writers. "All the experiments I am about to describe," he says, "were either performed before my eyes in the laboratory of the famous Roman College, or else were communicated to me by most reliable persons" (*11*).



The Alchemists' Furnace at the Roman College

From "Mundus Subterraneus."

Detailed and accurate descriptions of the furnaces used in the laboratories of the alchemists are now given, illustrated by excellent drawings and diagrams. Kircher describes the reverberatory, the calcinatory, the open, the closed, and many other types of furnace. The vessels used, the retorts, phials, and bottles, of clay, glass, and china are also described, and explanations of their various uses are given.

The following chapter, Kircher says, "is not just for the interest of the reader, but is to serve as a practical manual of techniques for the student." Here we find described methods of calcination and purification of metals, of precipitation, of sublimation, of solution, as well as what might be considered a very "modern" method of filtration. We are instructed to pour the suspension "through a filter, either of woolen or linen cloth, or through blotting paper folded or bent in the shape of a funnel; the residue will be left behind on the filter" (*12*).

The following chapters give prescriptions for various chemical preparations. We are told how to make various types of vitriol and other chemical substances. But for the archaic terminology used, the instructions might have been from an elementary text of today.

Kircher finishes this section by saying that "the above account of chemical preparations has been given to prepare the novice for further reading, by supplying him with sufficient chemical terms and methods" (*13*). He now feels that he can pass on to an elaborate examination of "The mystery of the Philosophers' Stone."

The Philosophers' stone, Kircher says (*14*), has been given many names: elixir, blessed earth, tincture, wood of life, etc.

> many of them ridiculous, others even blasphemous. The alchemists describe the stone as something wonderful and mysterious, which not alone can cure the human body of all ills and keep it healthy, but can also change base metals into gold and silver. . . . They say it is a pure, unchanging, most simple metallic substance, and that it is effective in infinitesimal amounts.

Far from believing such extravagant claims, Kircher bluntly states that most of what has been written about this "mystery" is a fraud and utterly useless.

There can be only one type of transmutation of metals, he continues, and this is to be learned from Nature, who "from the four elements generates the true principles, salt, sulphur and mercury, and from these, by correct proportions, produces trees, animals and all other material things" (*15*). Unless the alchemists imitate Nature and learn from her what is this "common matter" from which all other things are made, they will never make a success of their art of transmutation.

This reference to the "elements and principles" would seem to us to be in direct opposition to Boyle's teach-

ing in the "Sceptical Chymist." However, it is well to recall a passage in that book in which Boyle suggests that "earth by a certain metalline, plastic principle latent in it, may be, in the process of time, changed into a metal.... It seems evident that water may be changed into all the other elements.... Animals and plants may be produced out of water" (*16*). Boyle, however, did not think that it was necessary to postulate any "common matter," "any primogenial and simple bodies, of which, as from pre-existing elements, nature is obliged to compound all the others." He felt that nature could bring about such transformations of elements by "variously altering and contriving their minute parts" (*17*).

Kircher maintained that the alchemists had long sought this true "prime material." At various times they have described it in various ways; have said it was a metal, a salt, or some other such substance; have held that it is to be found in hair, in rotten eggs, in human blood, in dung, or in some other outlandish place. Some of them have even given a prescription for its preparation from the four "elements," from air, fire, water, and earth, by separation, conjugation, putrefaction, coagulation, fermentation, and other meaningless processes.

He quotes Paracelsus who used mercury as the starting point for preparing the "prime matter of all metals." Paracelsus claims that by following his prescription it is possible to convert the "calx" of any metal into pure quicksilver, which is the starting point for all other metallic transmutations. "Well spoken, indeed," says Kircher, "but when this theory is examined rightly, it is seen that it does not answer to practice...for I say that all you have at the end is the same mercury with which you began, a little purified by sublimation, perhaps. We have often demonstrated this process by experiment.... Therefore, what Paracelsus here promises is not true" (*18*). Kircher had discovered what is well known to every schoolboy chemist today: that mercury on heating in air is converted to an oxide, and that further prolonged heating will reconvert this oxide to mercury.

Another chapter of the book asks and, according to Kircher's ideas, answers the question, "can one metal really be transmuted into another?" Kircher holds that "in theory such a transmutation is possible, but in practice I think that it could only be accomplished with the help of angels or devils." This assertion may be either a heavy, seventeenth century joke, or the expression of the very real belief many had at the time in the power of magic. It is more likely the former, since Kircher himself was twice accused of sorcery and only with great difficulty succeeded in proving his innocence. Such an accusation was no light matter at a time when witches were still being hunted in England, Germany, and elsewhere.

Kircher agreed with Roger Bacon who has said that "metalline materials," or minerals, could be changed into pure metals, for, says the Jesuit, "as I have shown in the eighth book, lead, bronze, gold, silver, etc., can be changed by nature into other metals. This is possible because they all possess a common matter, a vapour or a tenuous something of a sulphureo-salino-mercurial nature." But the question is, he continues, can man achieve such transformations by his own arts? Paracelsus held that he could, though only with great difficulty, and he proposed some experiments to prove his assertion. "So let us examine some of these experiments" (*18*).

Paracelsus gave a method for making copper by boiling iron filings in dilute vitriol. But Kircher often tried this experiment and found that the "copper" is nothing more than the iron filings coated with a thin layer of copper. His explanation of this happening is that "the bronze hidden in the vitriol" (we would say, the dilute sulfuric acid contaminated by a minute amount of copper sulfate) "from its natural affinity to iron rushes to it and sticks to it" (*19*). It is an early example of the well known experiment of coating the steel blade of a knife with copper by plunging it into a dilute solution of copper sulfate.

Paracelsus' prescription for making lead from iron is similarly shown to be the result of the misinterpretation of the results of the experiment. Kircher's investigations have shown the inaccuracy of this claim also.

The last chapter in his book on alchemy carries the title: "Pseudochemistry—concerning the frauds, deceits and other means by which alchemists have pretended to make pure gold, and which even today they have not ceased to practice" (*20*). Kircher had first-hand information on such fraudulent practices. It seems that many tricksters, the "confidence men" of his day, used to come to him and try to sell him their prescriptions for making gold. They knew that he was interested in all sorts of curious things, and that he was reputed to be rather credulous. But their hoped-for dupe was too clever for them. He would let them go on explaining their methods until they had implicated themselves, and then show that he knew their frauds. The legal penalties for such trickery could be very severe, and it was not long before these men were appealing to Kircher for mercy. He thus compelled them to reveal their tricks to him, and then, as he says himself, he would "let them go with an admonition and an alms."

By such means he learned many of the secrets of their sleight-of-hand. One of these was the use of a hollow stick, plugged with wax and containing some gold dust. When they stirred their bubbling, boiling mixtures from which they claimed to be able to produce gold, the wax melted and the gold fell to the bottom of the vessel. Then, when their brew was ready, they showed their admiring audience the gold they had made.

Another of their tricks was to have the bottom of a metal vessel plated with gold and then covered with some soluble paint. When their gold-making mixture had boiled long enough, and they were sure that all the paint had dissolved off the bottom of the vessel, they emptied out the mixture and the gold-plated bottom was now revealed!

Thus ends the book on alchemy, the part of "Mundus

Subterraneus" in which we are principally interested.

FATHERS OF MODERN CHEMISTRY

In 1665 Henry Oldenburg, Secretary of the Royal Society and editor of its *Philosophical Transactions*, complained in a letter to Boyle that he had been forced to pay more than forty shillings for Kircher's "Mundus Subterraneus" (*8*). He feared that he had not got his money's worth, but I wonder whether Boyle agreed with him? Boyle must have felt that Kircher had answered his challenge of "The Sceptical Chymist" honestly, though perhaps without being aware that he was doing so. Boyle would have appreciated "Mundus Subterraneus," though he could not agree with everything in it. His own frequent, deferential references to the book in later writings show clearly his attitude toward its author. He certainly would have agreed with us in sharing, in some little way at least, "the fatherhood of modern chemistry" with Athanasius Kircher, the Jesuit Spagyrist at Rome.

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(10) *Ibid.*, p. 251.
(11) *Ibid.*, p. 256.
(12) *Ibid.*, p. 261.
(13) *Ibid.*, p. 267.
(14) *Ibid.*, p. 268.
(15) *Ibid.*, p. 269.
(16) BOYLE, R., "The sceptical chymist," in "Works," Vol. 1, pp. 563–4.
(17) *Ibid.*, p. 583.
(18) KIRCHER, A., "Mundus Subterraneus," Book 11, pp. 273 ff.
(19) *Ibid.*, p. 275.
(20) *Ibid.*, p. 299.

THIOACETAMIDE AS A SULFIDE PRECIPITANT IN QUALITATIVE AND QUANTITATIVE ANALYSIS

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IN SPITE of its dangerously high toxicity and objectionable odor, hydrogen sulfide has long remained an important reagent in most qualitative analysis schemes. In quantitative analysis the use of hydrogen sulfide has been considerably restricted, largely because of its tendency to form colloidal precipitates.

During the past five years, thioacetamide has been progressively replacing hydrogen sulfide in analytical laboratories. The reasons for this are not far to seek. Thioacetamide is a superior sulfide precipitant to hydrogen sulfide; furthermore, it possesses none of the physiological disadvantages of the gaseous reagent. It is the purpose of this paper to discuss the use of thioacetamide as a sulfide precipitant in both qualitative and quantitative analysis.

Thioacetamide, $CH_3—\overset{\overset{S}{\|}}{C}—NH_2$, is a white, water-soluble solid, m. p. 115–16°C. While both the solid and the aqueous solutions are stable at room temperature, the solution begins to hydrolyze rapidly at temperatures above 80°C. The hydrolysis, which occurs presumably through the thioenol form, $CH_3—\overset{\overset{S—H}{\|}}{C}=NH$, yields first acetamide and hydrogen sulfide, and finally further hydrolysis of the acetamide forms ammonium acetate.

$$CH_3—\overset{\overset{S}{\|}}{C}—NH_2 + H_2O \rightarrow CH_3—\overset{\overset{O}{\|}}{C}—NH_2 + H_2S$$

$$CH_3—\overset{\overset{O}{\|}}{C}—NH_2 + H_2O \rightarrow CH_3—\overset{\overset{O}{\|}}{C}—O^- + NH_4^+$$

Thioacetamide first achieved prominence as a fungicide in surface-decay control of citrus fruits (*1*). Its use as a substitute for hydrogen sulfide in qualitative

analysis was first suggested in this country by Barber and Grzeskowiak (*2, 3*).

THIOACETAMIDE IN QUALITATIVE ANALYSIS

In the use of thioacetamide as a substitute for hydrogen sulfide in precipitating Group II and Group III sulfides, no basic change in analytical procedure is required. In a typical case, to the filtrate from Group I, made approximately 2 *N* in acid, a slight excess of a two to five per cent solution of aqueous thioacetamide is added. The mixture is heated for five minutes on a water bath, at which time the pH is lowered to 0.5, and the sulfides of As, Sb, Sn, Hg, Cu, Bi, Pb, and Cu come down. An excellent description of a complete analytical scheme employing thioacetamide is given by Blomendal and Veerkamp (*4*). A textbook suitable for a one-semester introductory course in semimicro qualitative analysis has recently been published (*5*).

Experience has shown that a major analytical advantage of thioacetamide over hydrogen sulfide is that of the superior coagulative properties of the precipitates formed. This is particularly important at low metal-ion concentration where thioacetamide brings down a precipitate which can be easily filtered or centrifuged, whereas, under similar conditions, the precipitate with hydrogen sulfide is usually colloidal in nature. The ability of thioacetamide to precipitate sulfides quantitatively, in separable form, has made it suitable not only for macro and semimicro qualitative analysis, but also for microanalytical work. Detailed procedures for its use in microchemical work are given by Flaschka (*6*).

THIOACETAMIDE IN QUANTITATIVE ANALYSIS

Research on the use of thioacetamide in quantitative analysis has been largely carried out in Austria by Flaschka and his students.

Antimony (*7*) can be determined by precipitation of Sb_2S_3 from acid solution with thioacetamide. The precipitate is dried at 280–300°C. in a current of carbon dioxide. The procedure can be made volumetric by dissolving the Sb_2S_3 and titrating with standard bromate. The method is fast and accurate.

Bismuth (*8*) can be precipitated quantitatively as the sulfide, Bi_2S_3, from both acid and basic solutions, and in the presence or absence of CN^-, with thioacetamide.

In the determination of molybdenum (*9*), thioacetamide is much superior to hydrogen sulfide. The molybdenum sulfide is brought down quantitatively by heating with thioacetamide under slight pressure at 100°C. The sulfide is ignited to the oxide, MoO_3, before weighing.

Copper (*10*) can be precipitated rapidly and quantitatively with thioacetamide from hot acidic or ammoniacal solutions. The CuS is ignited to the oxide, dissolved in sulfuric acid, and titrated iodometrically.

Both As (III) and As (V) (*11*) can be determined quantitatively as sulfide with thioacetamide, from acidic solutions.

Cadmium (*12*), as the sulfide, can be brought down from either acidic or ammoniacal solutions with thioacetamide.

Lead (*13*) is first precipitated as PbS, which is dried at 110°C. Best results are obtained if the sulfide is oxidized to sulfate before weighing.

Tin (*14*) must first be oxidized to Sn (IV) before precipitation in acid solution as SnS_2 with thioacetamide. The authors recommend the addition of a small amount of mercuric chloride after precipitation.

In the determination of mercury (*15*), the sulfide can be precipitated from acid solution in a weighable form. However, high values are obtained, although these can be made quantitative by correction with an empirical factor.

In an excellent review paper Flaschka has summarized the results of his studies on the use of thioacetamide in quantitative analysis. Data are given on the precipitation of the sulfides of silver, thallium, mercury, copper, bismuth, lead, arsenic, antimony, tin, molybdenum, zinc, cadmium, cobalt, nickel, manganese, vanadium, and selenium.

COST AND SAFETY ADVANTAGES

Experience with thioacetamide in freshman chemistry laboratories under the author's supervision has shown that it is decidedly more economical than hydrogen sulfide, despite the fact that thioacetamide is by no means a cheap chemical. This economy results largely from the fact that only a slight excess of thioacetamide is required.

Since thioacetamide generates hydrogen sulfide *in situ*, where it is immediately consumed, little if any hydrogen sulfide escapes into the laboratory. The safety advantages over hydrogen sulfide are apparent.

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ORBITAL MODELS

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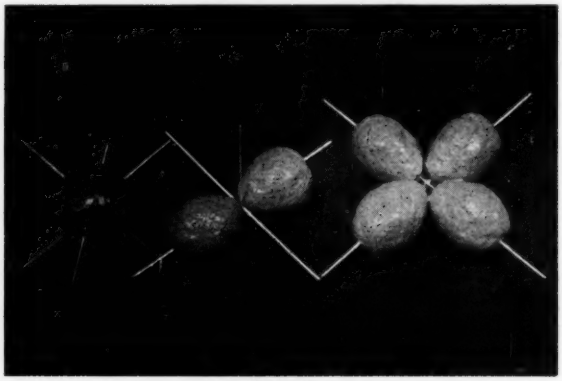

Figure 1

Left to right; s orbital, *p* orbital, and *d* orbital

MANY students find difficulty in appreciating the directional properties of atomic orbitals. They are told, for instance, of a *p* orbital which is symmetrical about the *x*, *y*, or *z* axis, and hybridized orbitals which may be linear, trigonal, tetrahedral, planar, or octahedral, to name only the more common; but despite tolerable blackboard sketches, the three-dimensional concept remains vague, and needs focussing by means of suitable solid models. How, then, can such models be made?

Balloons may, of course, be used to illustrate the hypothetical boundary surface enclosing say 90 per cent of the charge cloud, but balloons are notoriously shortlived and are not usually of the required shape (unless a group of balloons is used). Plaster of Paris models are possible, but lighter and far more robust orbitals can be modeled from *papier-mâché*. Photographs of some such models used by the author in teaching valence at Southampton are shown in the figures. These models have been made approximately to scale in agreement with Pauling's protrusion values[1]: An *s* orbital is thus a sphere of 1-in. radius (unit protrusion), while each lobe of the *p* orbital is about 1.7 in. in length. The orbitals have been distinguished by the following color scheme:

Simple Orbitals. The *s* orbitals are orange, *p* orbitals green, and *d* orbitals yellow.

Hybridized Orbitals are all given a basic black color, and are painted with rings the color and number of which correspond with the orbitals contributing to the hybrid. *E. g.*, *sp* hybrids have one orange and one green ring, sp^3 hybrids have one orange and three green rings, and d^2sp^3 hybrids have two yellow, one orange, and three green rings.

Models of simple molecules can also be made, when the orbitals will be molecular, embracing both the bonded atoms. These molecular orbitals are divided

[1] PAULING, L., "Nature of the Chemical Bond," Cornell University Press, 1945, p. 78.

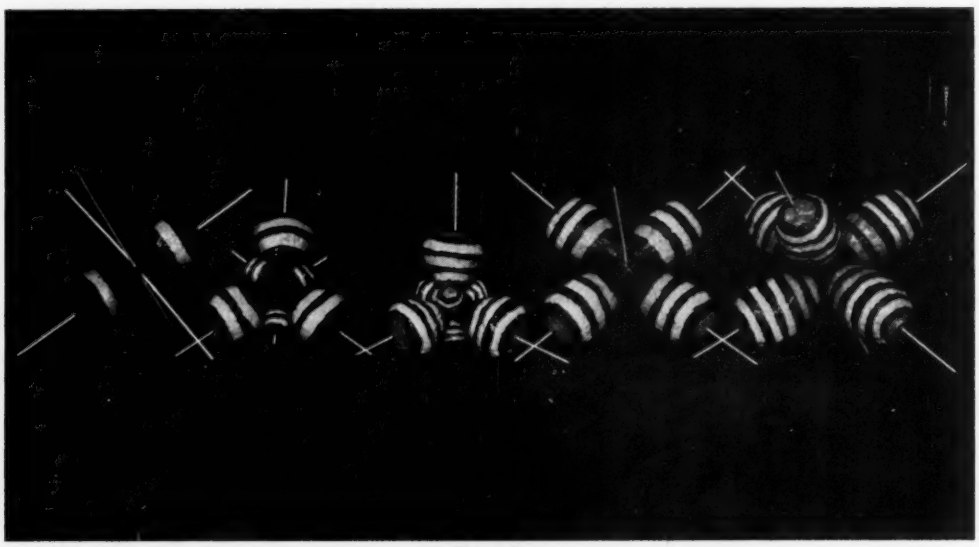

Figure 2

Left to right: sp hybrid orbitals; sp^2 hybrid orbitals; sp^3 hybrid orbitals; dsp^2 hybrid orbitals; d^2sp^3 hybrid orbitals

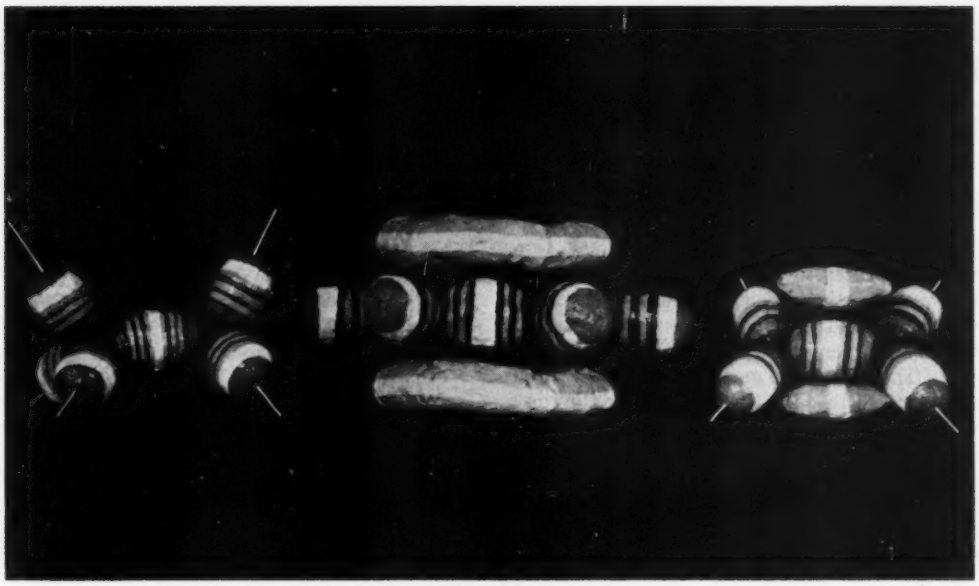

Figure 3

Left to right: ethane molecule, benzene molecule, and ethylene molecule

by a broad white band, and each half is painted according to the type of atomic orbital which originally contributed to the molecular orbital. Thus π molecular orbitals are painted green with a white central band, since they are formed from p atomic orbitals. Figure 3 shows photographs of models of the ethane, ethylene, and benzene molecules, illustrating σ, localized π, and delocalized π orbitals respectively.

The skeleton framework for any of these models is made from lengths of piano wire or welding rod (18 s.w.g.) silver soldered together and bent to the required angles. *Papier-mâché* can readily be made by pulping old newsprint (not glossy magazines); the pulp is squeezed by hand to the approximate shape, allowed to dry slowly, and the inevitable bumps are then removed with a coarse file or with a grind stone. A hole (of diameter slightly less than that of the wire) is drilled in the orbital, which is then forced onto the framework. Since the metal framework is made first, some orbitals in the molecular models cannot be forced into position in this way, but must first be cut longitudinally and then placed around the wire and bound together with fine copper wire. When the whole model has been assembled it is given a basic coating of cheap paint (to remove the absorbent properties of the paper), painted appropriately, and given a coating of clear varnish.

ACKNOWLEDGMENT

My thanks are due to Mr. E. W. Balson, B.Sc., who prepared the photographs for the figures.

THE NORRIS AWARD

THE James Flack Norris Award, given biennially by the Northeastern Section of the American Chemical Society, to an outstanding teacher of chemistry, goes this year to Dr. Harry N. Holmes, the retired head of the chemistry department of Oberlin College. It is largely the result of his efforts that Oberlin occupies a leading position among the liberal-arts colleges of the country in the accomplishments of its graduates in chemistry. His teaching has inspired an imposing list of successful chemists. His textbooks have been among those most widely adopted and he is well known for his research on valencies and in colloid science. Among his many other honors he is a past president of the American Chemical Society.

THE CHEMISTRY INSTITUTES

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CHEMISTRY institutes for college chemistry teachers, sponsored by the National Science Foundation and the A. C. S. Division of Chemical Education, will meet next summer at the University of Minnesota and Syracuse University. The Minnesota meetings will be in Minneapolis from June 13 to July 16, 1955, under the direction of Robert C. Brasted. The meetings at Syracuse will be from July 5 to August 12, with Edward L. Haenisch as director. The programs will in general follow the pattern of the institute in Laramie, Wyoming, last summer. As at Laramie, the programs will feature outstanding lecturers and discussion leaders.

Principal lecturers at Laramie included John C. Bailar, Jr., Farrington Daniels, Philip J. Elving, George Gamow, Joel H. Hildebrand, Willard F. Libby, Glenn T. Seaborg, Ernest H. Swift, and Gerrit Van Zyl, as well as officers of the Division of Chemical Education and representatives of the National Science Foundation and of industry.

The First Chemistry Institute was sponsored by the National Science Foundation, the A. C. S. Division of Chemical Education, and the University of Wyoming. It met on the Laramie campus from July 19 to August 20. The Conference of Teachers of High-school Chemistry, sponsored by the Fund for the Advancement of Education (Ford Foundation) and the University of Wyoming met there at the same time. In addition to their separate meetings, the two groups scheduled a number of joint sessions, and intermingled continually.

William E. Morrell and E. R. Schierz were director and associate director of the institute, while Elbert C. Weaver and Guy P. Franck were the corresponding leaders of the conference.

"Recent advances in the various fields of chemistry" was the theme of the meetings. Emphasis was on subject matter, chemistry itself, rather than on methods of teaching.

In general, each morning, Monday through Friday during the five weeks of the institute, was devoted to lecture and discussion of recent advances in some particular area of chemistry.

The program for most week-day afternoons included a lecture on recent advances, or on some other appropriate topic, such as lecture demonstration techniques.

Discussion groups were organized to consider various problems chosen by the registrants: content of general chemistry; content of high-school chemistry and integration with college chemistry; chemistry in general education; particular problems in the areas of high-school chemistry, organic chemistry, analytical chemistry, physical chemistry; chemistry in the junior college; undergraduate research; psychology of learning; etc. Each such discussion group met daily for two or three weeks.

For the most part, evenings were either left free or were devoted to motion pictures, lectures of a lighter nature, or entertainment. Wives and children participated in these evening programs, along with the registrants, and the same was true of the daily afternoon social hours. Saturdays and Sundays were left free for trips to nearby mountains and national parks.

Sixty-six registrants participated in the institute. (This number does not include staff, speakers, or University of Wyoming participants.) Of these, 42 stayed the entire five weeks. The other 24 attended from one day to four weeks each. Staff and speakers totaled 27 (some local), and an additional 22 registrants came from the University of Wyoming. Altogether, then, 115 college teachers from 72 schools participated in the institute. They came from 31 states, Washington D. C., the Hawaiian Islands, and the Philippines.

Expenses of 28 of the full-time registrants at the institute were paid from a fund from the National Science Foundation. Each high-school teacher registered at the conference received a $150 expense grant from money provided by the Fund for the Advancement of Education (Ford Foundation).

Fifty-six high-school teachers from 55 different schools in 16 states took part as registrants in the conference. Their four leaders, plus seven lecturers not otherwise listed (from industrial sources, etc.), brought the grand total of individuals who participated in the two meetings to 182.

More important than numbers and geographical distribution, however, are the reactions of the teachers who attended. At the close of the meetings the participants were asked to list comments and criticisms which could be used for guidance in future meetings. A department chairman of a liberal-arts college wrote: "After careful thought I feel the past five weeks have been the richest educational experience in any similar period of my life, and this includes many very excellent summer sessions at [leading universities]." A professor of chemistry at another well known liberal-arts college wrote: "Meeting these men and hearing them discuss recent developments in chemistry has been one of the most stimulating experiences of my teaching career (1925–54)." A professor of chemistry at a midwest state teachers college reported: "This institute has been the best thing professionally that I have partici-

pated in since my completion of graduate work. The organization of the institute and the nature of the program more than met my initial hopes." Another from a state teachers college: "I have never spent as profitable five weeks at any time or any place." A teacher from a university in the Philippine Islands wrote: "I found it to be the most wonderful experience I ever had! I can say with all sincerity that I have never been so inspired and challenged." A Catholic Sister, head of her department: "It was truly an unsurpassed educational experience." A junior-college instructor: "I thought it a *wonderful* meeting. It was inspirational, informational, and most enjoyable." Two high-school teachers: "The value of the joint meeting of the conference and institute groups has been inestimable." "Without doubt most of those participating will return to their work with a better understanding . . . and best of all a renewed respect for and pride in our profession."

Registrants were asked whether it had been of value or disadvantage to them personally to have the college and high-school groups meeting on the same campus at the same time, with some joint sessions. Both groups reported overwhelmingly that the plan followed (concurrent but separate meetings, plus the joint sessions) had been advantageous. A state-college instructor, for example, wrote: "This has been of greatest value to me. A chance to discover what goes on inside high schools without anyone feeling that you were feeling superior or critical of their work. A chance to find that both college and high-school people have similar aspirations, problems, and distresses can't be evaluated." A liberal-arts college man wrote: "The happy circumstance of a concurrent Conference of High-school Chemistry Teachers at Laramie made a fine contribution to the institute." High-school teachers expressed fervent appreciation of the presence of the two groups on the campus at the same time. One said: "This has been perfect. Here we've been accepted. We've been part of the gang instead of being 'the great Unwashed' as we're usually regarded."

Institute registrants were asked: "Would a program more like a usual summer school, with a smaller number of lecturers providing course-like offerings throughout the session, have been more or less advantageous than the plan that was followed?" Replies, by a ratio of more than ten to one, favored the plan followed. Some of the reasons advanced were: wide variety of speakers meets needs better and provides more stimulation; summer schools are already available for those who want work of that kind; Ph.D.'s would seldom go back to summer school; program of summer-school-like courses could not have achieved the coordination of the college and high-school groups that existed at Laramie.

The chemistry meetings, of which the institute in particular was a direct outgrowth, date back to the summer of 1950. At that time the Committee on Teaching of College Chemistry (a committee of the A. C. S. Division of Chemical Education) sponsored a ten-day "workshop" at Oklahoma A. and M. College. This was followed by similar meetings at Oklahoma A. and M. in 1951 and 1952, at Pennsylvania State College and California Institute of Technology in 1953, and at North Carolina State College and Kenyon College earlier in the summer of 1954.

Continuing this series, a ten-day conference for college and high-school chemistry teachers is scheduled for this summer at Fisk University, Nashville, Tennessee, in addition to the longer institutes at Minnesota and Syracuse universities. The National Science Foundation is also sponsoring similar institutes in the fields of physics, mathematics, and biology.

Academic credit will be available to registrants at the chemistry meetings who request it. A number of local sections of the American Chemical Society plan to pay expenses of teachers in their areas to attend the meetings. Expenses of other registrants will be paid by themselves or by their schools. Also, expense grants from the institutes will be available to a number of teachers who would otherwise be unable to attend.

Further information, beyond the announcements that will appear in THIS JOURNAL, *Chemical and Engineering News*, etc., can be obtained by writing: Dr. Robert C. Brasted, Director of Second Chemistry Institute, North Central Session, Department of Chemistry, University of Minnesota, Minneapolis 14; or Dr. Henry Wirth, Associate Director of Second Chemistry Institute, Eastern Session, Department of Chemistry, Syracuse University, Syracuse 10, New York.

SECOND SUMMER INSTITUTE

THE Second Summer Institute for Teachers of College Chemistry, Northern Section, will be held at the University of Minnesota from June 13 to July 16. Its particular aim will be to present modern theories and practices in the various fields of chemistry in such a manner as to facilitate their incorporation into the college curriculum.

The staff will be drawn from various departments of the University, from industries of the area, and well known guest speakers from other universities. Support from the National Science Foundation will make available stipends to help cover tuition and home costs. Information about these and all other matters pertaining to the institute may be had from Dr. Robert C. Brasted, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota. (See page 262.)

THE PURPOSE AND CHARACTER OF LABORATORY INSTRUCTION[1]

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IN ORDER to appreciate and understand the significance of laboratory instruction in higher education, it is necessary to go back several hundreds of years in the history of institutions of higher learning.

In the early years of the seventeenth century, laboratory instruction was beginning to take root in European universities. Johannes Hartmann of the University of Marburg is credited with offering the first practical exercises in chemistry in 1609, and with setting up the first university chemistry laboratory (*18*) ". . .in which his students also were allowed to work, but only for the making of pharmaceutical preparation. . . ." However, it was not until the early 1800's that modern laboratory instruction was offered: in Göttingen (from 1806 under F. Stromeyer); in Landshut (from 1807 under J. N. Fuchs); in Jena (from 1811 under J. W. Fisher).

Instruction in the natural sciences has been offered in American colleges for over 300 years. Astronomy and the "nature of plants" were offered at Harvard as early as 1690 (*1*). During the eighteenth century Yale, Princeton, and Columbia (then King's College) all offered work in natural history which covered physics, chemistry, geology, astronomy, botany, and zoology (*15*). By the middle of the nineteenth century instruction in the natural sciences became a very definite part of the college curriculum. The various sciences were being differentiated from each other, and separate courses were beginning to be offered in each. The first professor of chemistry in this country was appointed in 1768 at the College of the Province of New York (*2*). Chairs of chemistry were established at Princeton in 1795, at Columbia in 1800, at Yale in 1802, at Bowdoin in 1805, at South Carolina and at Dickinson in 1811, at Williams in 1812, and thereafter at most other recognized institutions.

Although the science curriculum was coming into prominence during this period, instruction was almost entirely by lectures and demonstrations on the part of the lecturer. Very few laboratories existed, and these were for the instructor and his assistants. President Eliot of Harvard wrote, in 1904 (*13*):

> When I was a student in the Harvard College there was not a single laboratory open to the students in any subject, either chemistry, physics, or biology. The only trace of such instruction open to students was in the department of botany and that was only for a few weeks with a single teacher, the admirable botanist, Asa Gray, and he had neither apparatus nor assistants, and it was a hopeless job which he undertook for a few weeks in May and June. I was the first student who ever had the chance to work in the laboratory in Harvard College and that was entirely due to the personal friendship of Professor J. P. Cook, who fitted up a laboratory in the basement of University Hall, entirely at his own expense. That was the situation of the colleges in the country—for Harvard was by no means peculiar in this respect—only sixty years ago.

One of the early efforts to include laboratory work by the student in the natural sciences took place with the establishment of Rensselaer Polytechnic Institute in 1825. In its science program students were required to lecture and perform experiments before the class as part of the required course work. The establishment and rapid growth of the land-grant colleges and universities with emphasis on practical applications to agriculture greatly increased the use of laboratory work as a means of training the student, but it was not until the beginning of the twentieth century that individual laboratory work for the student became common.

The first published catalogue of what was then Storrs Agricultural School states (*25*): "The first term, the Juniors spend four hours per week reciting Chemistry. It is sufficient time to enable them to learn how to make the different elementary gases; in fact to acquire a good understanding. . . ." It is not clear from the schedule how many hours were devoted to laboratory. However, by 1903 the pattern had been clearly established. In the course description of general chemistry is found (*24*): "Two hours of lecture and two two-hour laboratory periods." It is interesting that this pattern was strictly adhered to until the fall of 1946.

During the last 50 years laboratory work has become one of the most important and commonly-used procedures for instruction in science. "Science and experiment seem to have become almost synonymous terms." (*19*) Other areas of study outside of the natural sciences have also adopted the laboratory approach, and each year it becomes more widely used.

PURPOSE

In order to appraise laboratory work we must consider it in terms of its aims and objectives; to make an over-all inclusive statement of the aims of laboratory work in college science teaching is very difficult, if not impossible. Institutions have developed more or less independently and have built their curricula to meet their varied objectives. They have never been standardized to the extent of our secondary schools. This may well account for the paucity of articles on the fundamental problem of the function and place of laboratory instruction. However, there are at least

[1] Presented at Teachers' Seminar on Pharmaceutical Education, Storrs, Conn., August 18, 1954.

four broad functions: first, liberal-arts education (including general education); second, professional training (preparation of teachers, nurses, etc.); third, highly specialized or technical training (training of engineers, chemists, pharmacists, etc.); and fourth, the training of laboratory technicians for specific, routine jobs.

The problem of providing courses which meet the needs of all types of student in a college or university is difficult and often an administrative impossibility. However, it is now common to differentiate between courses taken as general education and those taken as preparation for further specialization. President Eliot said (*14*): "There are then two quite distinct functions which school and college laboratories perform. They tend to raise the observational powers of the average, and they give a chance to men of remarkable capacities to develop these capacities."

Many laboratory manuals state that the purpose of laboratory instruction is to bring the student into actual contact with the material studied. This enables the student to obtain a knowledge of the subject that mere study alone cannot furnish. Other contributions of laboratory work frequently listed are: development of manipulative skill, development of self-reliance and ingenuity, training in the accuracy of measurement and the interpretation of experimental data, training in the writing of satisfactory reports, satisfaction of curiosity, and the cultivation of scientific attitudes and an appreciation of scientific method through experimental investigation. It should be borne in mind that much that has been written about the scientific method is sheer verbalism, and that the scientific method does not follow a series of steps but consists of the use of innumerable and almost unclassifiable techniques. Hurd (*17*), in a study published in 1929, lists 43 functions of laboratory work in sciences as offered by 35 science instructors at the University of Minnesota. Some of the functions mentioned include: to give skill in using the scientific method, to develop manipulative skill, to aid memory, to develop power of observation, and to teach the student self-confidence. It is interesting to note that 19 of 33 teachers felt that these abilities could not have been developed by any procedure other than laboratory work, while 12 of the 33 thought they could be developed by other than laboratory procedures.

Much of what has been mentioned in the previous pages applies particularly to beginning or introductory courses. Advanced courses may well have certain aims peculiar to them which will determine their purpose and which must be left to the judgment of the instructors who teach them.

THE NATURE OF LABORATORY WORK

Laboratory work in its broad sense implies "learning by doing." Certainly this concept is in accord with the currently accepted theories of learning and has a good psychological foundation (*10*). However, it is important to remember that laboratory work should be conceived as a means to an end and not as an end in itself. Too often much laboratory instruction is routine, laborious, and uninteresting. "Much of the laboratory work done in our present system is open to serious criticism because in many cases it consists of little more than a pupil going through a set of motions following directions of a 'cook-book recipe' type" (*16*). There are, of course, certain special situations which may warrant the use of "cook-book" procedures, especially in the training of personnel for specific, routine tasks. This method was used very successfully during the last war, but it has little or no place in college work.

Good laboratory work should be motivated by a real need and should embrace the spirit of discovery. It should awaken a keen interest in both students and teaching staff. It should be an integrated part of the course work, and its relationship to the course should be clear to the student. It should involve both qualitative and quantitative aspects depending upon the particular problem at hand. And the attitude of the instructor is probably of crucial importance, since it in large part determines the "atmosphere and climate" of the laboratory (*9*). It is he who determines whether or not the laboratory work will achieve its purpose, or whether it will become dull and routine. Unfortunately, much laboratory work is conducted on the basis of the deductive-descriptive approach as represented by the typical laboratory manual. In the deductive approach the student starts with a principle and makes observations or performs experiments to verify what is already known. All too often the student can complete the exercise more accurately outside the laboratory. And unknowingly, instructors may be encouraging intellectual dishonesty by demanding too precise results. Many students begin their laboratory work with an enthusiasm which they soon lose when they must get the results expected rather than observe what is really going on.

In contrast to the deductive-descriptive, the inductive-deductive approach implies the use of observed data to arrive at a more general principle which is then used in solving specific problems. "By inductive teaching is meant progressing from the particular to the general or more specifically from facts to concepts and principles" (*23*). The laboratory period is used to gather data. Properly used, it can be a challenging experience. Unfortunately, this calls for expenditure of effort on the part of both the pupil and the instructor, and it takes time; and there are few, if any published, college laboratory manuals which employ the inductive-deductive approach. Fortunately, many of the standard laboratory exercises can easily be reworded in problem form so that this approach can be used.

It is not to be inferred that all laboratory work should be inductive. There is not time to rediscover all that has been discovered in the past; but a proper balance in the use of inductive and deductive procedures is needed. Bayles (*5*) has recently written a provocative article, "Is modern science inductive?" covering this very point.

Since the inductive-deductive approach requires more time, it leads directly to the problem of what proportion of the time allotted to a course should be de-

voted to laboratory work. A review of college catalogues indicates that the amount of time devoted to lecture and laboratory in science classes varies considerably. No studies have been found to indicate that there was any sound reasoning underlying these patterns. Local tradition or the whim of the instructors is apparently a determining factor (*3*).

Bowers reported a study of the importance of laboratory work as compared with textbook work (*8*):

> Students are allowed to take the textbook work for two recitation periods per week, with the privilege of taking laboratory work for one double period per week, and receiving four credit hours for one quarter's work in the course . . . . The two hour workers average 81.2 per cent and the four hour workers average 85.7 per cent. This gives a difference of 4.5 per cent in favor of the four hour workers. Since the four hour workers spent twice as much time in the laboratory and one-third more time on the subject as a whole, it might seem as though the last twenty-five per cent of the time was unprofitably spent.

Noll has reported on the results of an experiment, involving individual laboratory work versus oral quiz and recitation. In this study a combination of oral quiz and recitation was substituted for some of the laboratory work regularly scheduled in courses in general chemistry at the University of Minnesota. He concluded that (*20*):

> There is no evidence here to indicate that Group III-*b* was done any injustice by being given an hour of recitation and deprived of two hours of laboratory work. If it lost through this change in method of instruction, other measures must be devised to show it.

While the group having the oral quiz or recitation was superior in most cases, it did not differ from the control group by a statistically significant amount.

Noll has also reported on the results of an experiment involving two groups having identical instruction except for the number of hours of individual laboratory work. These two groups had the same three lectures per week, but Group IV-*a* had five hours of laboratory work per week—a two-hour period and a three-hour period, while Group IV-*b* was excused from the two-hour period. He concluded (*21*):

> Of forty-two differences between means . . . thirty-eight favor Group IV-*a* and only four favor Group IV-*b*. None of these differences is significant. . . . In summary it can be said that when two groups were compared on measures of final achievement, after two quarters of instruction that were identical except for the amount of laboratory work, the group having the more laboratory work was consistently superior in mean achievement and somewhat less consistently the more homogeneous of the two.

Ahmann has reported on a study conducted at Iowa State College. Students in one group were taught by the recitation-laboratory method, which consisted of six contact hours per week divided into three two-hour periods. Students in the other group were taught by the lecture-recitation-laboratory method which consisted of two one-hour lecture periods, two one-hour recitation periods, and one three-hour laboratory period. The mean score on the final examination for the recitation-laboratory group was 77.12 while the mean score on the same final examination for the lecture-recitation-laboratory group was 80.22. While the difference between the means is not statistically significant, the author concluded that (*4*):

> The two methods for teaching introductory chemistry to freshman students in engineering were considered to be equally satisfactory. Although the statistical analysis indicates the foregoing conclusion, the Chemistry Department considered many features of the recitation-laboratory method so desirable that they have been incorporated into the teaching methods of many freshman classes.

Blick (*6*) reported a study comparing three schedule patterns in teaching general chemistry involving different amounts of laboratory and lecture work. It was found that one three-hour laboratory period was superior to two two-hour laboratory periods.

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JOSIAH WILLARD GIBBS

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NAMESAKE of his father who was professor of sacred literature and ancient languages at the Yale Divinity School, Josiah Willard Gibbs was born at New Haven on February 11, 1839. After his graduation in 1858 he continued his studies at Yale, also teaching Latin and natural philosophy. From 1866 to 1868 Gibbs studied physics, chemistry, and mathematics at Paris, Berlin, and Heidelberg. In 1871 he was appointed professor of mathematical physics at Yale, holding this chair until his death on April 28, 1903.

The simplicity of the stone which marks his grave in the New Haven cemetery is thoroughly in keeping with his unostentatious way of life. His office furniture and papers are preserved in the Yale library.

Gibbs, who indisputably had one of the greatest minds produced in this country, owes his fame chiefly to his work in thermodynamics and statistics. "Graphical methods in the thermodynamics of fluids," and 'Method of geometrical representation of the thermodynamic properties of substances by means of surfaces" were his first contributions to the field. His masterwork on "The equilibrium of heterogeneous substances," appeared in two parts in 1876 and 1878. It was translated into German by Ostwald in 1891, and into French by Le Chatelier eight years later. In 1881 and 1884 his notes on the elements of vector analysis were printed for the use of his students; they later served as the basis of "Vector Analysis" by his student E. B. Wilson (1901). A series of papers on certain points in the electromagnetic theory of light and its relation to the various elastic solid theories appeared between 1882 and 1889, while his last great work, "Elementary principles in statistical mechanics," was published in 1902.

The English physical chemist F. G. Donnan, one of the editors of Gibbs' collected works, stated that "Gibbs ranks with men like Newton, Lagrange, and Hamilton, who by the sheer force and power of their minds have produced generalized statements of a scientific law which mark epochs in the advance of knowledge." Ostwald wrote:

> The importance of the thermodynamic papers of Willard Gibbs can best be indicated by the fact that in them is contained, explicitly or implicitly, a large part of the discoveries which have since been made by various investigators in the domain of chemical and physical equilibrium and which have led to so notable a development in this field.... The contents of this work are today of immediate importance and by no means are they of mere historical value. For, of the almost boundless wealth of results which it contains, or to which it points the way, only a small part has up to now (1892) been made fruitful.

Concerning what is probably the greatest work of Gibbs, namely, "The equilibrium of heterogeneous substances," the following comments are typical. Sir Joseph Larmor stated: "This monumental memoir made a clean sweep of the subject, and workers in the modern experimental science of physical chemistry have returned to it again and again to find their empirical principles forecasted in the light of pure theory and to derive fresh inspiration for new departures." H. A. Bumstead, one of the editors of the 1906 edition of the "Scientific Papers," wrote:

> To have obtained the results embodied in these papers in any manner would have been a great achievement; that they were reached by a method of such logical austerity is a still greater cause for wonder and admiration.... Some attempts had been made to bring chemical action within the scope of thermodynamical laws, but they had been successful only in a few isolated special cases; a way could not be found to open up the whole subject and obtain the broad general relation as had been done in the case of mechanical energy. The way seems easy enough now; but it is also easy to recognize it as just one of those

things which needs a stroke of genius to uncover it. It was Willard Gibbs who supplied this stroke of genius. He did more, however, than to open the way; in a single publication he carried the study of the relations between heat and energy of chemical combination to a degree of completeness equal to that of the older theory which dealt with mechanical work. The older theory had to do with a less complicated subject; it was the work of a number of men whose mathematical deductions were constantly being checked by experiment and who had the stimulus of mutual suggestions from each other's work. Professor Gibbs worked alone in a field in which he had no rivals and no helpers; he published practically all he had to say upon the subject in a paper of great length; and there were scarcely any experiments to which he could look for confirmation or suggestion as to his theoretical conclusions. Yet his very numerous results were

correct, were of the highest importance, and were extremely general in their application. Many things which had been mysteries, and concerning which our ignorance had been confessed by such vague terms as "affinity" or "catalytic action" were in this paper shown to be simple and direct consequences of the two laws of thermodynamics. Relations between facts and laws of chemical action were stated *a priori* which have since been verified by laborious and exact experiments; in fact there is little exaggeration, if any, in the statement that this paper contains, so far as general principles are concerned, practically the whole science which is now called physical chemistry and which had scarcely been begun when it was written. Considered merely as a *tour de force*, there are very few chapters in the history of science which can be compared with this; as an example of scientific prediction it is probably without a rival in the number and complexity of the relations discovered, by *a priori* reasoning, in a science essentially experimental.

Bumstead was fond of recounting a conversation that Gibbs was reputed to have had with a youthful investigator, who had made a laborious experimental study, and who was, with pardonable pride, telling Gibbs of his conclusion. After listening attentively he closed his eyes, thought a moment, and unaffectedly said, "Yes, that would be true," seeing at once that the special result which the young man had reached was a necessary corollary of Gibbs' own more general results.

Much has been made of Gibbs as the almost classic instance of a prophet without honor in his own country. There were good reasons for this seeming neglect. During his lifetime there were very few people who had the ability and desire fully to appreciate what he had done. Only a few special students were, of course, attracted to his lectures; the bulk of the men on the Yale campus were unaware of his existence, to say nothing of his greatness. He himself, shortly before his death, remarked that in his 30 years of teaching he had not had more than a half-dozen students with the ability and the preparation to profit fully from his courses. In other words, his influence was exerted almost entirely through his writings, and hence, when important sections of his work were published originally in an obscure journal, it is not surprising that due recognition of his outstanding accomplishments was long delayed. Furthermore, like many an exceptional man, he was in advance of his generation; he simply was not understood. But when understanding did come, chemists and physicists from all the civilized world were eager to pay him proper tribute. For instance, when Lord Kelvin was in New Haven in 1902 he said that he would willingly have made the trip over here for the satisfaction of talking with Willard Gibbs. Not many Americans were then capable of appreciating the accomplishments of their distinguished countryman, but Europeans like Ostwald, Planck, Huggins, and Ramsay were alike in their praise. One of the members of the Connecticut Academy, in whose *Transactions* Gibbs published some of his most important papers, confessed that none of that body was able to appreciate their importance or real significance. "We knew Gibbs and took his contributions on faith." It is interesting to speculate what the effect would have been had the paper been refused and Gibbs forced to seek a more accessible medium.

The fiftieth anniversary of the publication of the first part of his great work on the equilibrium of heterogeneous substances was honored by issuance of a Gibbs number of the *Chemisch Weekblad* (**23**, 405 (1926)).

It contained contributions by Dutch, Norwegian, German, French, Canadian, and English authorities, but none from an American. However, honorary degrees were awarded by Williams College, Princeton, and also by Erlangen (Germany) and Christiania (Norway). The Rumford Medal of the American Academy of Boston was received in 1881 and the Copley Medal from the Royal Society in 1901. Many learned societies both in this country and abroad elected him to membership. Lectureships and a medal in his honor are continued in this country.

Although no more purely theoretical mind ever existed than his, the practical applications of his work have been varied and extensive. Among the industries profiting from his work are cement, ores, fertilizers, fuel and power engineering, metallurgy, colloids, and chemical manufacturing. The phase rule has been termed a veritable Rosetta stone in the solving of the problems presented by highly complex salt mixtures. It has been well said that the value of Gibbs' work to industry has been great enough to pay for a large part of the research undertaken in the physical sciences.

The reputation of Willard Gibbs has not waned with the passing years; in fact, quite the opposite is true. Many of the advances in physical and other branches of chemistry are little but applications and variations of the fundamental concepts that he outlined many years ago. It apparently has required a long time for Americans to realize that he will be numbered among the most renowned theoretical scientists of all time, but at long last the greatest American honor has now been shown him. After unsuccessful previous attempts, in 1950 he was elected to the Hall of Fame. However, the funds are still lacking to provide the bronze bust for the colonnade on the New York University campus. Perhaps it is therefore especially fitting to point out now that not only did the German chemist-physicist Walther Nernst give Yale University the funds for erecting a memorial plaque in the Sloane physics laboratory, but that none other than Lord Kelvin said, when visiting at Yale, "By the year 2000 this university will be best known for having produced J. Willard Gibbs."

ERRATUM

In the article "Experiments on reflectance measurements," in our February issue, the captions for Figures 5 and 6 were reversed.

A DEMONSTRATION FOG CHAMBER

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With an increasing interest in subatomic phenomena there has been a corresponding interest in demonstrating the characteristics of radioactivity for the general student. With this in mind the author has devised an instrument, based upon the fog-chamber technique, which serves as a classroom tool for instruction. More than a score of students may observe the fog tracks simultaneously. In view of the economical construction of the instrument, as well as its dependability in operation, it is presented here as a guide for others who may wish to construct one for use with their own classes.

The fog chamber is essentially a glass-enclosed box in which there is a region of supersaturated vapor of a suitable liquid. The region of supersaturation, sometimes called the sensitive layer, may be two or three centimeters thick, although usually it is somewhat thinner. In this region any charged particle emanating from a radioactive substance causes molecules of the air to become ionized, which in turn serve as nuclei for the precipitation of vapor, thus forming a visible fog. The resulting fog track marks the trail of the radioactive particle. Wide fog tracks indicate alpha particles and narrow tracks are formed by beta particles. If a track suddenly appears to start at some distance from the radioactive substance, this may be caused by a gamma ray which strikes a molecule, ejecting a charged particle which then forms a fog track. Cosmic rays also produce fog tracks in the sensitive layer.

The instrument is made primarily of two components. First, a glass-walled, cubical box of approximately one foot on each edge (Figure 1). The box is constructed of grooved 1-in. × 1-in. stock and ordinary window glass. The top of the box is removable; a pad is attached to the underside of the top panel to which a liberal quantity of isopropyl or ethyl alcohol is applied when the instrument is operated. A wire screen is attached to the underside of the top panel; it is attached to one side of a high-voltage supply. The other side of the high voltage is attached to the bottom of the box which is a piece of sheet metal painted black on its upper surface. The box is supported on a frame in which a slab of dry ice is placed. A one-inch slab of dry ice provides a sensitive layer in the instrument for a period of about two hours. An alternative to constructing a glass-walled box is to use the case from an ancient or otherwise useless analytical balance, a supply of which frequently adorns the back corner shelves of many academic storerooms. In this instance, a sheet-metal bottom should be substituted for the stone base of the balance case.

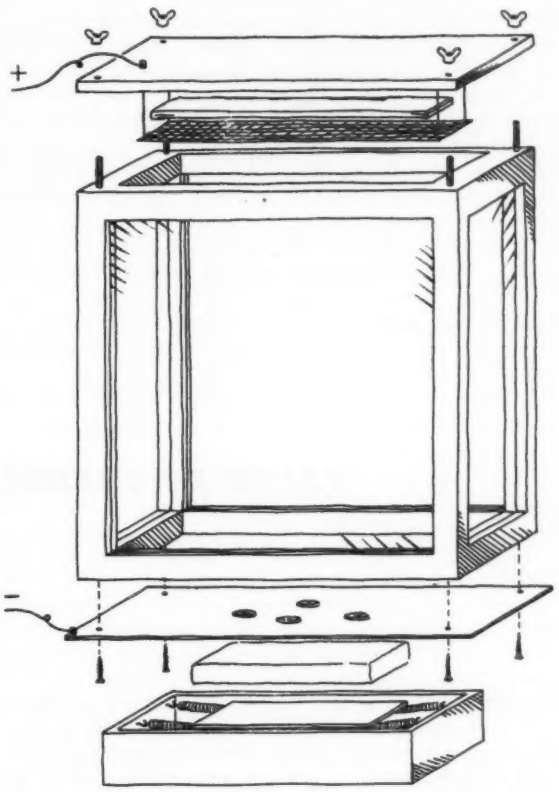

Figure 1

The second component is a high-voltage supply. The circuit diagram of the power supply constructed for this instrument is shown in Figure 2. As a precaution it is well to remember that the voltages produced in such a power supply are potentially hazardous; they should be used carefully. The purpose of the electrical field superimposed upon the vapor system is to sweep out excess ions that otherwise serve as fog nuclei. Ideally, only those ions created by the radioactive emanations should give fog nuclei.

In operation, several samples of radioactive salts such as uranium and thorium nitrates are placed on the floor of the fog chamber. Each sample is individually mounted on a thin slice of a rubber stopper, and coated with a lacquer or cement which resists the alcohol that condenses upon the floor of the chamber. The fog chamber is adequately illuminated with a single desk lamp placed next to one side of the box. The fog tracks

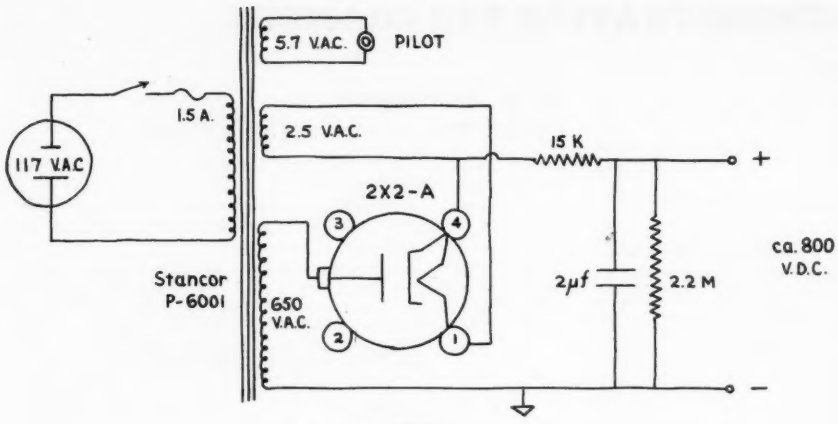

Figure 2

are visible through all four sides of the box, but appear most intense when viewed from the side opposite the lamp. The fog chamber will operate continuously as long as there is a supply of alcohol and dry ice. As many as four or five fog tracks may be simultaneously visible to the observer.

ACKNOWLEDGMENT

Acknowledgment is given to the kind assistance of Mr. D. N. Montan in constructing the high-voltage supply.

FAITH IN CHEMICAL RESEARCH[1]

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IT CERTAINLY is a privilege and an honor to share with you in this Joseph Priestley Celebration, for our ties overlap to some extent. Priestley and Lavoisier were contemporaries, and not only with respect to discovering oxygen and indentifying it as an element, for Lavoisier was also E. I. du Pont's chemistry teacher. Then his eldest son and the second president of the du Pont Company—Alfred Victor du Pont—attended this college where you so highly honor Priestley's legacies, both chemical and spiritual.

As God-fearing Americans, as businessmen and educators, as teachers and scholars, we are constantly challenged to balance the new against our traditions. Much in our past has gone with the wind never to return except as museum pieces and treasured antiques. On the other hand, we must never outgrow humility, honesty, hard work, frugality, fair play, sobriety, and the cooperative spirit. To balance properly the best of the old with the best of the new is difficult for the wisest and most prudent of men. Your college education should certainly help you in this respect but rightly discerning the truth is one lesson that is never completely learned.

Priestley and Lavoisier complied with several important patterns that still guide our best and newest research efforts. Priestley discovered oxygen, but it was Lavoisier who first recognized it as an element and thereby dealt the death blow to the phlogiston theory. This early spirit of scientific collaboration is one of the main reasons for the phenomenal progress of all chemical and physical research. To this day "Na" is the symbol for sodium in all languages, "K" stands for potassium, and so on through the periodic system. As a matter of fact, the language of science comes as close to being an international tongue as any speech has ever been. At the world meeting of chemists in New York City in 1951, leading teachers and research workers came from every part of the world and were probably as well informed as to what was being done here as we are as to the latest results coming from the laboratories of India, Germany, Sweden, etc. Thus, long before the concept of the League of Nations or the United Nations, the scientists of the world had been speaking a more or less

[1] Presented at a student assembly at Dickinson College, Carlisle, Pennsylvania, in connection with the Priestley Celebration and the presentation of the Dickinson College Award in Memory of Joseph Priestley, April 22, 1954.

common language and perhaps setting the stage for a better understanding between nations. If this be wishful thinking, then let us at least dedicate our efforts as chemists, teachers, and students to this end.

Undoubtedly, Priestley's true greatness as a scientist was his ability to penetrate the unknown. Most of us have trouble enough understanding and remembering what others have done, but to stand so high above our contemporaries that our vision penetrates the haze of accepted theories and the maze of everyday problems is a gift that is rare indeed. The principle may be simple and the experimental procedure fairly crude, but if a new world is discovered, lesser men will certainly fill in the details. Oxygen is so essential to chemistry that the weights of all other elements are related to its weight of 16. The simple problems of metals versus their oxides—which excited much of Priestley's curiosity—laid the foundation for our steel industry, whereby the oxygen combined with iron is removed by roasting with carbon. But this principle would not work with aluminum oxide, so many years passed before the electrolysis of bauxite ($Al_2O_3 \cdot nH_2O$) in molten cryolite (Na_3AlF_6) gave birth to the aluminum industry. In turn, this principle would not work on titanium, so more years passed before this was done commercially. This is a process I will describe in some detail later on.

In passing, however, it might be worth our while to consider a few more simple but fundamental discoveries that have shaped the world of science and altered the course of human affairs. Near the top of the list should be the observation that an electric current is generated when a loop of wire is moved across a magnetic field. Little did Faraday foresee that he was laying the groundwork for the great and small motors and generators that play a major role in our modern civilization.

Many were those who laughed at the idea of an orderly arrangement of the elements, but a strong argument can be written on the thesis that Mendeleev's periodic system laid the foundations of our modern concept of atomic structure. This and the discovery of radioactivity were the forerunners of our atomic age.

To change the setting somewhat, Newton's development of calculus is one of the greatest contributions to pure reason and clear thinking that the human mind has ever devised in the realm of theoretical science. To apply this powerful tool to the solving of maximum-minimum problems is perhaps the apex of a college education. It is almost like handing a student a magic key to the world's storehouse of scientific theory. To this day, a workable knowledge of calculus makes the study of almost all college science an easy matter, since this is usually the stumbling block of those students who have trouble with sciences in college.

Pasteur must be included in any listing of the world's great scientists. So must de Forest for his invention of the controlled-grid vacuum-tube amplifier, Gibbs for his development of thermodynamics, and G. N. Lewis for his modern concept of acids and bases.

This is but a partial list, but it does illustrate the fact that the world of science, as well as today's civilization, has been shaped by the discovery of a relatively few simple but basic concepts.

The search for novel ideas, unbridled collaboration, and faith are still the basic principles underlying scientific progress, even though the size and scope of the research effort have grown tremendously over the past few years. Colleges, universities, research institutes, industry, and government are providing huge sums of money to support many thousands of highly trained scientists. An essential part of this vast effort is to provide an academic atmosphere that eliminates the drive for production and the pressure of competition. In other words, surroundings and incentives are provided so that men can think and work together as a team in search of those simple, fundamental principles which are so elusive and yet so essential to true progress. Do not assume that this is done for the sheer love of scientific progress; experience has shown time and time again that such faith—or some call it a "gamble"—is a wise and profitable investment. Such fundamental studies account for approximately 20 per cent of, for instance, the du Pont research dollar; the remainder is spent on the development of existing ideas and the further refinement of chemicals and processes to fit the exacting requirements of the ultimate customer. For example, the research chemist may consider his job done after he has discovered a new polymer, be it a new textile fiber, an improved rubber, or a more durable paint film. The engineer must develop a practical process for manufacturing this new product in good yield, of excellent quality, and at a price to meet competition. The sales development group must then devise a means to handle this new product in existing plant equipment or develop new equipment to do a better job; for always the final product must be superior if it is to enjoy lasting success.

Let me illustrate with one of our classic examples and a couple more that may not be as well known to you. Chemists were puzzled and challenged by the excellent behavior of rubber, silk, cotton, linseed oil paints, wool, wood, and many other natural products. Chemists tried and tried again but always failed to approach the excellent properties of these common materials, much less exceed their performance. Then Dr. Wallace H. Carothers got the idea that a very pure difunctional molecule with a negative group built on each end (much like two negative magnets attached to each end of a link) would form an almost endless chain-like molecule if it were combined with another pure difunctional molecule with a positive group on each end. This very simple idea certainly rates with the great chemical discoveries of our generation, but it involved many disappointments and untold hard work before the principle was proved. Dr. Carothers' basic idea gave birth to nylon and, I think it is fair to say, contributed to an understanding of the entire field of polymerization. Synthetic rubbers, paints, textile fibers, and plastics are examples of

such polymers which owe their beginning to this simple discovery. The records show that Dr. Carothers began his research program in 1928, but it was 1940 before the first earnings on nylon were realized. In the meantime, $6,000,000 had been spent on research and development and $21,000,000 for operative investment in the face of what appeared to be virtually insurmountable obstacles. This illustrates the kind of faith that has made big companies successful and America strong.

Some years ago we learned that our company was buying several millions of dollars worth of a chemical from a small chemical company for use as a polymer intermediate. After several years' work our group was able to make a slightly better product by a somewhat improved process. An economic analysis of the over-all picture showed that while we could supply a somewhat better product at a somewhat lower cost, nevertheless the advantages were not such as to justify displacement of an existing source of supply. Therefore, our top management told us to use our money and research facilities to do what the other fellow could not do. This was a well-deserved slap and quite a disappointment to us at the time, but it has proved to be a fortunate decision in the long run.

This occurrence caused us to put more emphasis on the manufacture of pure $TiCl_4$ as an intermediate to other titanium products. On paper this appears to be the simplest of chemical reactions. The idea was to react chlorine and carbon with a naturally-occurring mineral, known as ilmenite, which is a mixture of titanium and iron oxides; the resulting chlorides could then be separated and purified by fractional distillation. Operating on a large scale with highly corrosive liquids and gases at high temperatures proved to be a most refractory chemical and engineering problem, ranking in difficulty, perhaps, with certain problems of the atomic energy plant at Hanford. Again, many millions were spent before the problem was solved and, again, there were many dark moments when we thought that the whole idea was unworkable.

But the story does not end here. Having a source of pure $TiCl_4$, we were now in a position to attempt the production of pure titanium metal. As stated previously, the known means of producing iron and aluminum would not work in the case of metallic titanium. At this point we must give credit to Dr. Wilhelm Kroll for developing a small-scale process for producing titanium. This is based on the reaction of $TiCl_4$ with metallic magnesium at very high temperatures. The resultant product is a sponge of metallic titanium containing by-product $MgCl_2$. This is removed by distillation and leaching and the sponge is then melted to an ingot of pure titanium. It now appears that this new metal is of vital importance to our national defense and for other uses that require a high strength/weight ratio and excellent corrosion resistance. Titanium is as strong as stainless steel, half as heavy, and as resistant to sea water as platinum.

These, then, are a very few examples of the type of problem that big companies can undertake and solve. Or, to put it differently, du Pont spent $57,000,000 in 1953 on research. This is a lot of money and it requires a lot of faith to invest such a sum in the search for new things, especially when you know the chances for major new discoveries are often very low. Of course many problems are studied for a short while and then discarded. Not more than about one out of five research dollars pays off, and only one out of twenty projects proves to be of commercial value.

Nationally, the research expenditure is tremendous—at an all-time high. It is estimated that during 1953 four billion dollars was spent on research—$2\frac{1}{2}$ billion by the government and $1\frac{1}{2}$ billion by private industry. This amounts to about $1\frac{1}{2}$ per cent of our national income, and is certainly a concrete expression of our nation's faith in research.

But if this were the extent of our faith our plight would be sad indeed. Again we can return to Priestley's example: this time, the spiritual heritage mentioned before. Here was a true scientist whose first allegiance was to God; here was an experimentalist who kept an open mind toward findings in the laboratory as well as things of the spirit. It is heartening to report that Priestley's spirit is alive today. There has been a 70 per cent increase in church membership during the past generation, which has outstripped the population growth by two to one. This argues well for the point that Americans know, even as President Eisenhower recently expressed it, that all our armed strength and technological prowess is not a safe citadel in these days of warring ideologies. We must believe in and practice the brotherhood of man and the fatherhood of God with greater vigor and certainty than our opponents support the supremacy of the state and the deity of superman.

America is great because our forefathers came here seeking freedom: political, personal, spiritual, and geographical. To be sure, we have been blessed with fertile fields, rich mines, abundant forests, and friendly shores. All this has led to the development of the nearest approach to heaven on earth that man has ever known. But all this we owe entirely to God, and if we owe any debt to our fellow men it is to help them attain the same freedom for developing their own ideals.

Certainly there will be no relaxation in our scientific effort but this must be matched by a determination to use this knowledge and power with all the wisdom that a humble and God-fearing people can muster. This is everyone's task and not one of us can or should avoid the responsibility. If you can balance the best of the old with the best of the new, the years ahead should bring each of you a sense of hard work, unbounded opportunities, and happiness.

• • •

LECTURE DEMONSTRATIONS OF INCENDIARIES. II[1]

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[EDITOR'S NOTE: We publish this with some trepidation, fearing that careless or irresponsible persons may try these experiments without proper regard for safety. *These experiments can be dangerous unless all the precautions are strictly observed.*]

GUNPOWDERS

To this category belong mixtures of sulfur, carbon, and an oxidizing agent. Regular gunpowder consists of a mixture of 75 per cent potassium nitrate, 15 per cent charcoal, and 10 per cent sulfur. The products formed after exploding the mixture are 44 per cent gaseous and 56 per cent finely divided solids. The composition of the remaining solid residue is approximately: potassium carbonate 60 per cent, sulfate 15 per cent, sulfide 13 per cent, and uncombined sulfur 12 per cent. In 1856 Lamont du Pont invented blasting powder in which he substituted the more readily obtainable Chile saltpeter (sodium nitrate) for potassium nitrate. Various types of gunpowder are listed in Table 1 together with gunpowder-type mixtures to which additives have been added to impart certain properties to the explosions resulting. Small quantities of the materials (the entire mass not exceeding 250 mg.) listed in Table 1 may be safely exploded by placing the powders on bricks and hitting them with a hammer. When preparing explosive powder mixtures three general safety rules should always be kept in mind.

(1) Use small quantities of material.
(2) Mix, *do not grind* the components.
(3) Keep rooms well ventilated.

COMBUSTION IN SULFUR DIOXIDE

Place a little magnesium in a deflagrating spoon. Ignite and insert the spoon's contents in a bottle containing sulfur dioxide. The magnesium burns vigorously, decomposing the SO_2. Powdered tin, antimony, lead, and iron will also burn in the gas, but not so intensely as magnesium. Hot, brown lead peroxide glows brightly in SO_2 and is converted into white lead sulfate. The reaction taking place is simply:

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

ZIRCONIUM

This metal is far superior to magnesium as an incendiary. However, its tendency to ignite when finely divided precluded its use as such during World War II. Zirconium powder is readily ignited by static electricity. To demonstrate this, place a pile of $^1/_2$ g. of powdered zirconium on an asbestos mat. Take a comb and run it through the hair. Bring the comb within half an inch of the pile. The static electricity produced ignites the zirconium which burns vigorously and spontaneously. Best results are obtained on dry days. Other sources of static electricity may be used as desired. It is best not to gaze directly at the burning metal. It is advisable for the instructor to wear smoked glasses when performing this experiment. The reaction is:

$$Zr + O_2 \rightarrow ZrO_2$$

NITRIC ACID

Add 24 ml. of concentrated sulfuric acid together with 16 ml. of concentrated nitric acid to a 1000-ml. beaker. Slowly drop in several drops of turpentine. The drops will burn vigorously upon contact with the acids. Add a few drops of nitric acid (conc.) to a pile of sawdust. The sawdust ignites instantly. The acid will also cause piles of finely divided metals and some metallic carbides to burn.

SODIUM PEROXIDE

One gram each of aluminum powder and sodium peroxide are mixed and placed together on an asbestos

[1] For the first paper in this series see J. CHEM. EDUC., **30**, 134 (1953).

TABLE 1
Gunpowders

Common name	*Composition*			
Amidogene	Potassium nitrate (70%)	Sulfur (15%)	Charcoal (10%)	Magnesium sulfate (5%)
Azotine	Sodium nitrate (75%)	Sulfur (15%)	Charcoal (5%)	Petroleum (5%)
Berthollet's powder	Potassium chlorate (85%)	Sulfur (10%)	Charcoal (5%)	
Blasting powder	Sodium nitrate (75%)	Sulfur (15%)	Charcoal (10%)	
Carbazotine	Potassium nitrate (70%)	Sulfur (15%)	Charcoal (10%)	Ferrous sulfate (5%)
Gunpowder	Potassium nitrate (75%)	Sulfur (15%)	Charcoal (10%)	
Red fire	Strontium nitrate (86%)	Sulfur (7%)	Charcoal (7%)	
Saxifragine	Barium nitrate (86%)	Sulfur (7%)	Charcoal (7%)	

TABLE 2
Ammonium Nitrate Explosives

Common name	*Composition*			
Amide powder	Ammonium nitrate (75%)	Potassium nitrate (15%)	Charcoal (10%)	
Amatol	Ammonium nitrate (80%)	TNT (20%)		
Ammonal I	Ammonium nitrate (72%)	Aluminum powder (16%)	TNT (12%)	
Casteau's explosive	Ammonium nitrate (90%)	Nitrodextrin (10%)		
Explosive P	Ammonium nitrate (90%)	Nitrocellulose (10%)		
Fractorite	Ammonium nitrate (70%)	Potassium dichromate (15%)	Rosin (10%)	Dextrin (5%)
Schneiderite	Ammonium nitrate (90%)	Nitronaphthalene (10%)		
Umbrite	Ammonium nitrate (38%)	Nitroguanidine (49%)	Silicon (13%)	

mat. A few drops of water allowed to fall on the mixture will ignite it. Sodium peroxide forms an explosive mixture with sodium thiosulfate which can also be ignited with water. Keep at a distance when igniting aluminum peroxide mixtures.

HOT IRON

Heat one end of a flat iron bar (at least $^1/_8$ in. thick and $^1/_2$ in. wide) over a Mecker burner until it is white hot. With gloved hand or tongs, hold the bar with the glowing end about half an inch above the surface of several drops of water placed on a strip of sheet metal. Strike the bar with a hammer, forcing the hot iron suddenly down upon the water. A loud explosion is produced together with a beautiful pyrotechnic display. The hot part of the iron bar is torn to shreds, causing sparks of molten iron and oxide to fly in all directions. What causes this beautiful display is a combination of several factors: (*a*) Water is suddenly vaporized to steam; (*b*) steam thus produced reacts with the hot iron giving magnetic iron oxide and hydrogen; (*c*) liberated hydrogen explodes; and (*d*) the heat of the exploding hydrogen causes a vigorous reaction to take place between the iron and the oxygen of the air in the vicinity.

Caution: Keep combustible material out of range of the flying sparks.

AMMONIUM NITRATE

This compound, which was responsible for the atom-bomb-like destruction of Texas City in 1947, owes its power as a high explosive to the fact that it yields no solid residues upon explosion. It is used in large quantities commercially in the manufacture of Amatol, and to a lesser extent in the manufacture of Ammonals. The Ammonals are a class of explosives consisting of NH_4NO_3 and aluminum powder to which is added a combustible material. Table 2 lists some ammonium nitrate explosive mixtures. It is best to mix small amounts of these materials and to ignite them, for explosion by friction tends to confine the gases produced (which are voluminous in comparison to same weights of gunpowders exploded) creating a safety hazard.

ORGANIC CHLORATES

Various organic substances when mixed with potassium chlorate form powerful explosive mixtures. Before performing the following experiment, it is advisable to open all doors and windows in order to achieve adequate ventilation. On an asbestos mat place a sheet of 12.5-cm. filter paper. In the center place 750 mg. of $KClO_3$ in a small mound. Add a little nitrobenzene to the crystals until they appear wet. Allow a little of the nitrobenzene to form a small liquid path to the edge of the filter paper so as to form a fuse. Light a match to the nitrobenzene and run to a safe distance. It is advisable to empty the first two rows nearest the lecture table if this experiment is used for demonstration purposes. No danger will result if these instructions are carried out. It is suggested, however, that the instructor attempt this demonstration (as well as the others mentioned here) prior to its presentation, so as to determine for himself the best safety precautions. This mixture of $KClO_3$ and $C_6H_5NO_2$ is commonly called Rackarock and belongs to a class of explosives known as Sprengel explosives (named after the inventor who perfected a class of explosives which could be manufactured and stored without danger). Table 3 lists some organic chlorate ex-

TABLE 3
Organic Chlorate Explosives

Common name	*Composition*			
Cheddite 60, No. 4	Potassium chlorate (79%)	Nitronaphthalene (1%)	Dinitrotoluene (15%)	Castor oil (5%)
Comet powder	Potassium chlorate (85%)	Rosin (15%)		
Himly and Von Trutschler Falkenstein's powder	Potassium chlorate (85%)	Powdered nutgalls (15%)		
Marantesite	Potassium chlorate (83%)	Methylcellulose (5%)	Nitrobenzene (12%)	
Oriental powder	Potassium chlorate (85%)	Gum gambier (15%)		
Pyrodialites	Potassium chlorate (80%)	Coal tar, charcoal (5%)	Nitrated hydrocarbons (15%)	
Rackarock	Potassium chlorate (80%)	Nitrobenzene (20%)		
Rosselite	Potassium chlorate (85%)	Asphalt oil (15%)		
White powders of Augendre and Pohl	Potassium chlorate (85%)	Cane sugar (10%)	Potassium ferrocyanide (5%)	

plosives. The same instructions given for igniting ammonium nitrate explosives should be employed when dealing with these mixtures.

ORGANIC NITRATES

Organic material mixed with potassium nitrate produces explosives which are strong but inferior to organic chlorates. This is the result of the fact that chlorates are in general superior to nitrates as oxidizing agents. Himly's powder is a mixture of hydrocarbons and KNO_3. It is easily prepared by saturating one g. of KNO_3 with petroleum ether, and following the same procedure as described for the ignition of Rackarock. Haloxyline is prepared by mixing 600 mg. KNO_3 together with 100 mg. sawdust, 50 mg. charcoal, and 50 mg. potassium ferrocyanide. The mixture is ignited on an asbestos mat and should not be confined.

ZINC STEARATE

Take a quantity of zinc stearate powder and place it in the palm of the hand. Blow the powder into a Bunsen burner flame. The rapid combustion of this powder produces a vivid flash of light accompanied by a harmless "woof."

LOST AND GONE FOREVER

PRACTICAL experience in dismantling a reactor is a new development in nuclear technology. Two reactors that failed have been disassembled—and one has been repaired and returned to operation—without exposing personnel to dangerous levels of radiation.

Within two weeks in December, 1952, the Canadian "NRX" reactor at Chalk River, Ontario, and the U. S. reactor affectionately known as "Clementine" at Los Alamos, New Mexico, were shut down. Clementine, a "fast neutron" research reactor, had been misbehaving since March, 1950, a year after it had gone into full operation. A uranium spacer rod had ruptured, and uranium and plutonium had contaminated the mercury used to cool the reactor. After the fuel rods had been replaced, corrosion and other changes in metal parts of the reactor continued, but the reactor remained in operation. Finally, the coolant again became contaminated, this time through the rupture of a plutonium fuel rod; an estimated one to ten grams of plutonium were free in the cooling system, producing a serious hazard from plutonium poisoning.

Following these troubles, Clementine was closed down and careful steps were taken to dismantle it without exposing personnel to danger from radiation and without contaminating the reactor building. Most of the disassembly was done with rubber gloves sealed to tightly covered "dryboxes," in which a vacuum assured that any leaks were inward. Vinyl plastic bags were used to transfer contaminated material from the reactor to disposal areas. This plastic protected workers against "alpha" radiation from the plutonium and served to keep plutonium dust from escaping. The entire operation was done without exposing personnel to more than a fraction of the tolerable dosage of radiation, and only a barely detectable amount of plutonium escaped.

In the case of the Canadian installation, the breakdown was more sudden and conditions more critical. Improper operation of the control rods caused a rapid reaction that burned out the aluminum sheaths covering about 10 per cent of the uranium rods in the reactor; melting and oxidation of the uranium released 10,000 curies (an extremely high level of contamination) of radioactive fission products to the cooling water. Contamination spread through the entire building housing the reactor and to the associated equipment.

The NRX installation is vital to the Canadian production of isotopes; it is also one of the most advanced in the world, and permits some unique experiments because it is one of the world's most intense neutron sources. Therefore it was decided to repair the reactor and clean up the radioactivity, rather than to abandon the installation, as in the case of Clementine. The difference in the cost and size of the two reactors was also a factor—Clementine was 11 by 15 by 9 feet, while the Canadian reactor housing was 35 feet high, and the reactor tank alone was ten feet high and eight feet in diameter.

PRECAUTIONS NECESSARY

The first and most pressing problem was to dispose of a million gallons of "hot" water. It was first stored in the process-water reservoir (thereby contaminating the reservoir) until a $1^1/_4$ mile pipeline was installed to carry it to a disposal area. The pipeline also carried off the water used in cleaning, as it became contaminated.

The reactor vessel, weighing $2^1/_2$ tons, was damaged beyond repair; this had to be removed by personnel wearing elaborate protective clothing and carefully checked respirators, to reduce the amount of skin contamination and ingested radioactivity. The already excellent ventilating system of the area was upgraded and men were allowed to work for only short periods of exposure to radiation. The concrete housing of the reactor was contaminated to an average of 10 roentgens per hour, and some local hot spots were as high as 3000 r. per hour. (Five hundred roentgens is a fatal dose; 0.3 roentgen per week is the permissible dosage for life-long exposures.) Most of the surfaces could be cleaned by scrubbing, scraping, grinding, sandblasting, or chipping. Continuous mopping and vacuum cleaning of all working areas removed the contaminated material as it came off. In some of the more difficult cases, when the activity had been reduced to 0.02 roentgen per hour the area was then sealed by pouring in fresh concrete as a shield. A unique method for detecting local hot spots was the use of a pinhole camera to take two pictures—one with light on optical film, and the other with gamma rays on x-ray film. Superimposed, the two negatives showed where high levels of radioactivity remained.

By February 1, 1954, the reactor had been restored to full operation, with 33 per cent higher power output than before. It would have cost four times as much, and taken three times as long, to replace it, and the rebuilding process gave valuable information for the design of new installations. But perhaps more important to the task of learning to live in the atomic age, there was no dangerous exposure of personnel, and not a single accident. —*Reprinted from the Industrial Bulletin of Arthur D. Little, Inc.*

THE DAWN OF HOT ATOM CHEMISTRY

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IT IS a matter of common observation that many important discoveries are preceded by anticipatory observations which, for a variety of reasons ranging from the lack of pertinacity of the investigator to sheer bad luck, fail to grow into the mature achievement of the recognized discovery. The episode I wish to describe is somewhat akin to this, although the anticipation takes the form of a verbal speculation rather than a laboratory observation. The evanescence of the spoken word must be my justification for putting it on record; certainly many of those who heard it are no longer living.

As a schoolboy of seventeen I was taken by my father who was a member of the organization, to a meeting on May 13, 1919, of the Manchester Literary and Philosophical Society. As an unusually youthful visitor at a meeting of a learned society of which John Dalton had been secretary, I should have been excited regardless of the topic under discussion. But this was to be something of an occasion because Sir Ernest Rutherford, then professor of physics at Manchester University, was to be presented with a Dalton medal and was to deliver a paper entitled "Recent evidence on atomic nuclei." As it turned out, the occasion was historic—and the paper highly appropriate for a recipient of a Dalton medal—because in it Rutherford made the first public announcement of the breakdown of nitrogen nuclei by alpha particles. In a passage beginning, "An interesting effect was observed in passing alpha particles through dry air...," he described the long-range scintillations that could only be accounted for by disruption of the nitrogen nuclei.

All this is well known. What I wish to record is a question put to Rutherford in the subsequent discussion by a member named Varley (like my father a high-school teacher of science and, as it happens, father of the present Hope Professor of Entomology at Oxford University). Varley asked simply: "What happens to the other nitrogen atom in the molecule when its partner is transmuted?" Rutherford's reply, which I do not profess to remember word for word, was roughly as follows: "Oh, well, in terms of the size of the atomic nuclei you have to imagine the other nitrogen atom as miles and miles away." The matter was pursued no further and the general impression was that Rutherford had tolerantly disposed of a rather pointless question.

In retrospect the question seems—at least to me—to be perhaps the first speculation as to the possibility of chemical change arising from a nuclear transformation, now the subject of so many interesting investigations. The time was not ripe for the observation. When it is recalled how little we knew about the covalent bond in 1919 the cause of this unripeness will be apparent. An unknown chemist was addressing to the great physicist an untimely (and distinctively chemical) question.

Perhaps I may conclude this note by seeking to preserve for posterity an observation that Rutherford made at least once in my hearing and, I suspect, enjoyed making from time to time in a genial vein when he found himself in chemical company. Like many another physicist—and with more justification than most of them—Rutherford liked to poke fun at the characteristic preference of most chemists for experimentation rather than abstract thought. On this occasion he was talking to the Oxford University Alembic Club, somewhere around 1930, and remarked with a twinkle in his eye: "If you chemists would only work less and think more, what *tremendous* strides we might hope for in your science in the next few years!"

BROOKHAVEN SYMPOSIUM IN BIOLOGY NUMBER 8: MUTATION

THE annual summer conference sponsored by the biology department of the Brookhaven National Laboratory, Upton, New York, will take place from June 15 through 17, 1955. Those planning to attend should notify Dr. R. C. King at the above address by May 21. If you are not a citizen of the United States, please indicate your nationality.

PORPHYRINS IN PETROLEUM

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University of Illinois, Urbana, Illinois

Porphyrins are nitrogen-containing pigments of biological origin and are intimately related to the iron-containing hemoglobin in the blood of animals and the magnesium-containing chlorophyll in the leaves of plants. Porphyrins can be considered to have been derived from the parent substance called *porphin* which has the heterocyclic structure of four pyrrole nuclei united by four methine (—CH=) groups (Figure 1). Imido porphins containing —N= groups instead of —CH= groups have been synthesized. Porphyrins encountered in the plant and animal kingdoms are derivable from porphin by the substitution of various groups like methyl, ethyl, vinyl, carboxylic, for the hydrogen atoms of pyrrole nuclei. They are probably flat molecules in which a slight oscillation of the metal will cause a rhythmic shift of all double bonds, making it a dynamic molecule. Usually metal atoms like Fe, Mg, Cu, Ni, V, are held between the four nitrogen atoms of the four pyrrole nuclei of the porphyrin molecule.

The porphyrin structure is stable. The occurrence of porphyrins in coal, bitumen, shale oils, petroleum, etc., is quoted as evidence in support of their organic origin. Porphyrins combine with many proteins and form complexes with metals. These porphyrin metal complexes play very vital roles in the living cell as respiratory pigments (hemoglobin), oxidation catalysts, photosynthetic agents (chlorophyll), etc. They are very widely distributed in nature (*1*, *2*, *3*).

Porphyrins are crystallizable and deeply colored substances; their color depends on the nature of the solvent, concentration, and the pH value of the solution. In general, porphyrin solutions are brownish-red in alkalies, red in neutral solvents, and purplish-red in acids. These color changes are closely linked with alterations occurring in the structures. They are freely soluble in many organic solvents like pyridine and petroleum. Porphyrins exhibit a great tendency to form colloidal dispersions in electrolyte-free media; they have well marked absorption spectra in the visible region; they have intense red fluorescence in ultraviolet light, and act as photosensitisers. Adsorption chromatography is ideally suitable for the separation and identification of porphyrins.

DISCOVERY AND ROLE OF PORPHYRINS IN PETROLEUM

In 1934, Triebs reported the discovery of the presence of porphyrins in petroleum (*4*, *5*). Later Skinner, and Moore and his co-workers (*6*, *7*) identified vanadium- and nickel-porphyrin complexes in petroleum.

Of the many substances possessing interfacial activity and film-forming tendency so far isolated from petroleum, like naphthenic acids, mercaptans, thiophene, and quinoline derivatives, the metal-porphyrin complexes are among the major contributors to the interfacial activity and film-forming tendency exhibited.

The discovery of the porphyrins in petroleum is a significant milestone in the study of the origin of petroleum. Skinner isolated a vanadium-porphyrin complex from Santa Maria Valley crude oil and found it to be interfacially active and film forming at a benzene-water interface. Moore, *et al.*, (*6*, *7*, *8*) have obtained nickel-porphyrin complexes and a smaller amount of the vanadium complex from a California crude oil and have correlated the film-forming tendency of the crude oil with the presence of metal-porphyrin complexes.

These remnants of chlorophyll and hematin in petroleum are proving to have great practical interest in several aspects of the petroleum industry. Because of their surface-active and film-forming properties, they affect the wettability of petroleum reservoir surfaces and thus influence the flow of liquids in these reservoirs. They may indicate the source beds of petroleum and petroleum migration from the studies of trace elements and porphyrins. Because many of these metal-porphyrin complexes are extremely stable, they introduce complications in the analysis of core samples and in the formation of stock tank emulsions in the field. Further, the porphyrin complexes cause the poisoning of the catalysts employed for cracking petroleum and are carried over into certain refined petroleum

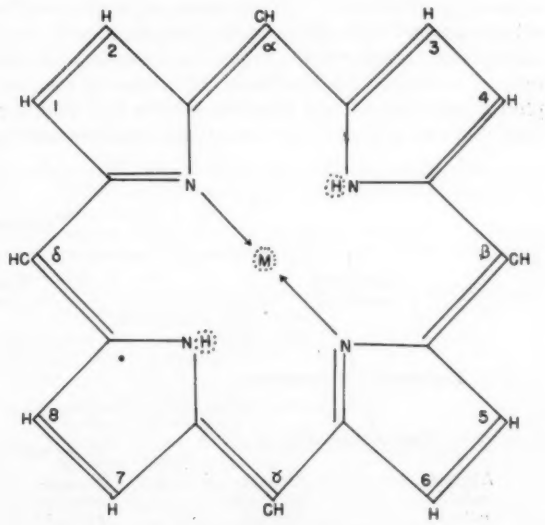

Figure 1. Porphin Structure

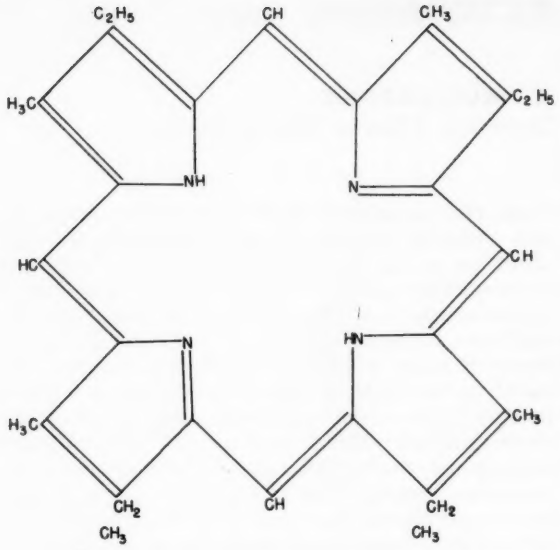

Figure 2. Etioporphyrin

products where their presence is undesirable or positively harmful. They thus produce harmful effects in the processing and utilization of petroleum (*6*, *7*, *8*).

EXTRACTION OF PORPHYRINS FROM CRUDE PETROLEUM

The scheme of extraction of the surface-active and film-forming substances containing porphyrins, porphyrin-metal complexes, oxidized porphyrin rings, and their metal complexes and protein-metal complexes, etc., is indicated in the diagram. Water-spray extraction is used at first to concentrate the porphyrin-containing substances from crude petroleum oils. Pentane extraction of the aqueous extract has been found to be very effective in the separation of surface-active substances and those containing nitrogen, nickel, vanadium, and porphyrins. There is considerable difference between the interfacial activities of the porphyrin aggregates from pentane-soluble and pentane-insoluble extracts and this indicates a good separation of relatively polar and nonpolar porphyrins by the pentane extraction (*7*). Further, the pentane-insoluble portion of the water-spray extract has been successively extracted with hexane, isooctane, cyclohexane, and benzene, and their spectra have been studied. The spectra of the alcoholic extracts of pentane-soluble and pentane-insoluble portions indicated the presence of metal-porphyrin complexes.

PURIFICATION OF PORPHYRINS

Recently Groennings has devised a method whereby porphyrin aggregates in petroleum can be determined. He extracted them into hydrogen bromide in glacial acetic acid and then transferred them to chloroform before transmittance was measured at the two characteristic wavelengths of 5000 and 5300 Å. (*9*).

Kennedy has devised a special apparatus for the fractional separation of eluates in the chromatographic separation and identification of porphyrins (*10*). Also, quite recently Kennard and Rimington have obtained methyl esters of carefully purified porphyrins by chromatographic techniques. They have classified and identified porphyrins by X-ray diffraction studies (*11*).

ABSORPTION SPECTRA

The absorption spectra of porphyrin aggregates found in petroleum are characterized by four major maxima in the visible region. The etio-porphyrin and phyllo-porphyrin spectra are of interest in studying porphyrins from petroleum. It must be clearly understood that even though the porphyrins prepared from chlorophyll have spectra of the phyllo-type and those prepared from hemoglobin commonly have spectra of the etio-type, there are a few exceptions to this generalization—the root nodules may contain hemoglobin and thus give rise to spectra of the etio-type. Calculation based on this concept showed that there is about two and a half times more plant porphyrin (phyllo-type) than animal porphyrin (etio-type) in the porphyrin aggregate from crude oil (*8*). Thus we get not only an idea about the organic origin of petroleum but also we can visualize the proportionate plant or animal origin of a sample of petroleum.

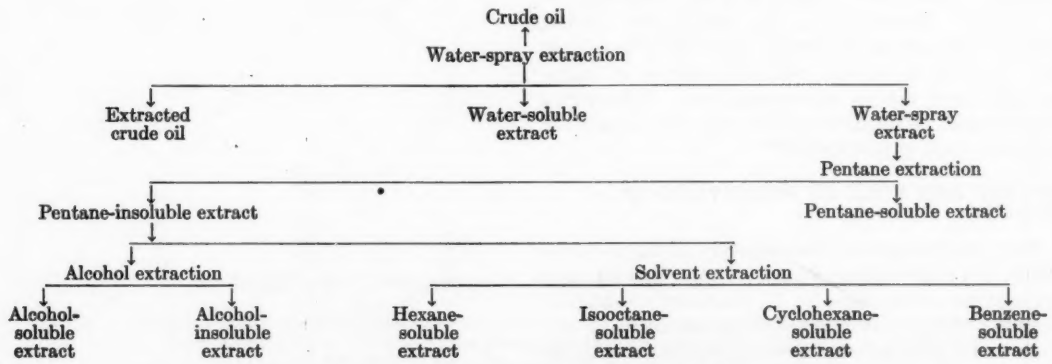

Diagram of Extraction Process of Petroleum for Porphyrin Recovery

THE INFRARED SPECTRA OF PORPHYRIN

The infrared spectra of porphyrin aggregates from the whole crude oil, pentane-soluble, and pentane-insoluble extracts show an absorption peak at 5.8 microns. This is tentatively thought to be due to the carbonyl radical (Figure 3). The spectra of other extracts do not show this 5.8-micron absorption peak but show other peaks at 3.5, 6.9, 7.3, etc. Probably this indicates that porphyrins having a carboxyl group like phyllo-porphyrin (Figure 3) are extracted from the crude oil by the water-spray process rather selectively. This has been verified by experiments.

ACIDITY AND INTERFACIAL ACTIVITY OF PORPHYRINS

The acidity of the porphyrin aggregates from the whole crude oil indicated a considerable content of interfacially active porphyrins. Since much of the interfacial activity of the porphyrins is due to their carboxylic-acid side chains (Figures 2 and 3), etioporphyrin having no carboxyl group would not be expected to be very active interfacially. But in a complexed form or in case the porphyrin molecules are vertically orientated at the interface, attractions between metallic constituents may stabilize the film (*8*).

SPECTROSCOPIC EVIDENCE FOR PORPHYRIN-METAL COMPLEXES

Microchemical analysis of crude-petroleum samples reveals the presence of Zn, Cu, Ni, Ti, Mg, V, Fe, etc. They are probably present as oil-soluble compounds, possibly as porphyrin-metal chelates or complexes with nitrogen-containing compounds. The film-forming fractions of petroleum appear to consist of proteins, waxes, and resins stabilized by orientated porphyrin rings, and the surface-active fractions may contain free porphyrins, porphyrin-metal complexes, oxidized porphyrin rings and their metal complexes, and protein-metal complexes (*6*).

The pentane-insoluble portion of the water-spray extract of crude petroleum was successively extracted with various organic solvents as indicated in Figure 3. The final extract gave a major absorption peak at 550 mμ and a weak absorption band at 510 mμ, and these indicate the presence of nickel-porphyrin complex (*8*).

Moore, *et al.*, actually synthesized a nickel-porphyrin complex from the porphyrin aggregates isolated from petroleum and nickel acetate. The absorption maximum of this synthetic product and that from the natural petroleum extract are identical. Thus the presence of nickel-porphyrin chelate in petroleum has been established (*7*).

The final extract also gave a weaker peak at 570 mμ and a weak absorption band at 530 mμ; these are caused by the presence of vanadium-porphyrin complexes (*8*).

CONCLUSION

Thus, crude petroleum has been found to contain nickel- and vanadium-porphyrin complexes, and the surface- and film-forming activity of the petroleum largely result from the presence of these complexes. The study throws light on the probable origin of petroleum. The study of porphyrins in petroleum has stimulated the interests of petroleum engineers, chemists, and those concerned with biology, surface active substances, film-forming agents, etc. This is one more example to show how the discovery and solution of problems in a particular field prove to be of great theoretical and practical value to workers in diverse fields.

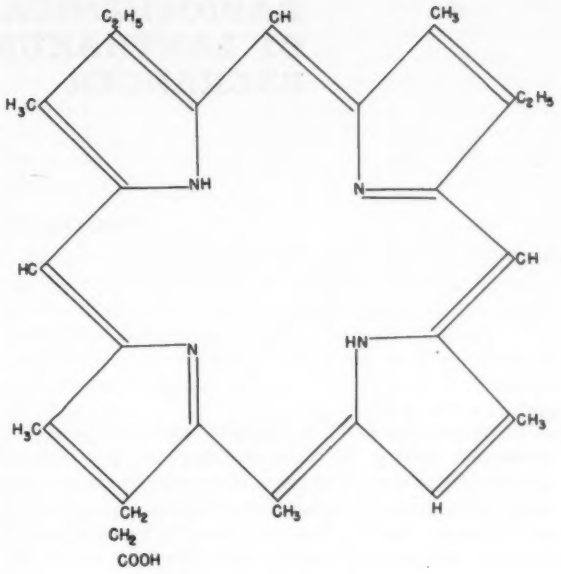

Figure 3. Phylloporphyrin

ACKNOWLEDGMENT

The author is grateful and thankful to Professors John C. Bailar and Therald Moeller, University of Illinois, Urbana, for helpful suggestions and advice in the preparation of this manuscript.

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RADIOCHEMICAL STUDY OF THE SEPARATION OF LANTHANUM FROM BARIUM BY CATION EXCHANGER

Genetic Study of Ba^{140}–La^{140} and a La^{140} Reservoir

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THE experiment described in this paper is designed for a laboratory course in radiochemistry or in advanced physical chemistry. The use of ion-exchange chromatography as a chemical tool is demonstrated. The experiment can be used to illustrate the genetic relationship between radioactive nuclides and effective use of discrimination in counting.

The experiment consists of the separation of the 40-hr. La^{140} daughter from its 12.8-day Ba^{140} parent by chromatographic elution from an ion-exchange resin column. The radiations from the two separated fractions are measured to show the decay of the 40-hr. La^{140} in the lanthanum fraction and the growth of 40-hr. La^{140} in the barium fraction. From two to three hours are required for the experiment. Further information can be obtained by making subsequent elutions at weekly intervals.

The elaboration of ion-exchange separation techniques for similar elements has played an important role in the development of modern radiochemistry (*1*, *2*, *3*). The place of such techniques in a course in radiochemistry or nuclear chemistry has been discussed elsewhere (*4*). The experiment outlined here has added interest because it deals with the decay chain Ba^{140}–La^{140}—the subject of study that led to the discovery of nuclear fission by Hahn and Strassmann (*5*)—and it is a prominent and very useful fission product (*6*, *7*).

The 12.8-day Ba^{140} is readily available from cyclotron-produced fission[2] or from the Isotopes Division of the U. S. Atomic Energy Commission or other national producers. It decays (*7*, *8*) by the emission of β rays (60 per cent at 1.0 m. e. v. and 40 per cent at 0.5 m. e. v.), and γ rays of medium energy (0.5 m. e. v.) are associated with the low-energy β rays. The 40-hr. La^{140} decays by the emission of harder β rays of several energies, and several γ rays, the most prominent being an intense component of 1.60 m. e. v. A thin-window Geiger-Müller counter is slightly more sensitive to the β rays of La^{140}, but use of sufficient absorber to cut out all β rays leads to 14-fold greater sensitivity for the γ rays of La^{140} (*9*).

[1] Present address: Nuclear Science and Engineering Corporation, Post Office Box 10901, Pittsburgh, Pennsylvania.

[2] The separation of Ba^{140} from uranium and the other fission products (neutrons or charged particles impinging on uranium targets) is described by L. E. Glendenin (*10*) for carrier-free samples, and (*11*) for samples with small amounts of carrier.

THEORY

The genetic relationship between two radioactive nuclides can be determined by observing the gross decay and growth behavior of the nuclides after chemical separation. The daughter nuclide always decays with its characteristic half-life. The behavior of the purified parent nuclide depends on the relative half-lives of parent and daughter (*6*, *8*). If the half-life of the parent is greater than that of the daughter, there is an increase of activity in the parent fraction. Transient equilibrium results when the decay of the daughter is balanced by its growth from the parent. Both activities then decay with the parent's half-life. If the parent is shorter-lived than the daughter, the sample decays and no equilibrium is attained.

The general equation which describes the growth and decay of a radioactive daughter nuclide from an initially pure parent is given as:

$$A_d = \frac{\lambda_d}{\lambda_d - \lambda_p} A_p^0 (e^{-\lambda_p t} - e^{-\lambda_d t}) \qquad (1)$$

where A_d is the activity of the daughter at time t, A_p^0 is the initial activity of the parent, and λ_d and λ_p are the decay constants of the daughter and parent respectively. If the parent is longer-lived than the daughter ($\lambda_p < \lambda_d$) equation (1) reduces for large t to:

$$A_d = \frac{\lambda_d}{\lambda_d - \lambda_p} A_p^0 e^{-\lambda_p t} \qquad (2)$$

since $e^{-\lambda_d t}$ becomes negligible compared to $e^{-\lambda_p t}$. The ratio:

$$\frac{A_d^0}{A_p^0} = \frac{\lambda_d}{\lambda_d - \lambda_p}$$

may be obtained by extrapolating the curve for A_d of equation (2) to $t=0$ (the time when the parent was pure).

For the parent-daughter pair 12.8-day Ba^{140}–40-hr. La^{140}, the initial growth of La^{140} activity is about 1.6 per cent per hour referred to A_p^0. The maximum La^{140} activity appears at 5.6 days after the isolation of radiochemically pure barium. Transient radioactive equi-

librium is approached in about 10 days, after which the La^{140} radiations decay with the 12.8-day half-life of Ba^{140}. Exact values may be computed from equation (1).

The separation of the daughter and parent nuclides can be accomplished by *ion-exchange techniques*. In the ion-exchange process a solution containing the cations to be separated is run through a conditioned column of cation-exchange resin. These cations exchange with the resinate cation (*e. g.*, NH_4^+) and are absorbed by the resin. The separation is then accomplished by removing the cations absorbed at the top of the resin column with a suitable eluting agent (*e. g.*, a complex-former) which moves them down the column at different rates.

The affinity of a cation for the cation-exchange resin generally increases with increasing valence when the concentration of the external solution and the cross-linkage of the resin are not too high. In addition, the fraction of cation bound by cation exchanger is reduced by complexing action (*1*, *2*), thereby reducing the time of a separation.

Because of the difference in ionic charge between a rare earth and an alkaline earth, a large difference is obtained in their rate of chromatographic elution (*12*) even under nonequilibrium conditions.[3] Further enhancement of their separation is made by taking advantage of the difference in complexing action of citric acid of the rare-earth and alkaline-earth elements.

Citric acid dissociates by the scheme:

$$H_3Cit \xrightarrow{-H^+} H_2Cit^- \xrightarrow{-H^+} HCit^{--} \xrightarrow{-H^+} Cit^{-3} \quad (3)$$

Its dissociation is very dependent upon hydrogen-ion concentration (*14*). Any one of the three citrate anions is capable of complexing cations. Although the higher charged citrate anions usually form the stronger complex ions (*15*), it is convenient to express the complex formation occurring in fairly acid solutions (around pH 2.5) as one involving H_2Cit^-. The main reactions are then:

$$M^{+3} + 3NH_4R = MR_3 + 3NH_4^+ \quad (4)$$

where M^{+3} represents a trivalent rare-earth cation and R an equivalent of resin anion, and:

$$M(H_2Cit)_3 = M^{+3} + 3H_2Cit^- \quad (5)$$

The mass-action constant for equation (*4*) is $K_{exchange}$ and that for equation (*5*) is $K_{complex}$. It is customary to represent the gross partition ratio between resin and solution as K_d. Within the limitations of this treatment[4] it can be shown that:

$$K_d = \frac{K_{exchange}K_{complex}}{K_1^3}\left(\frac{NH_4R}{NH_4^+}\right)^3\left(\frac{H^+}{H_2Cit}\right)^3 \quad (6)$$

The dependence of K_d upon the pH and the ammonium-ion concentration is illustrated by equation (6). Since a decrease in the hydrogen-ion concentration is accompanied by an increase in the ammonium-ion concentration, K_d will decrease rapidly as the pH increases.

The rare earths are strongly complexed by citrate solutions at pH<3 (*12*, *16*) in the form of $M(H_2Cit)_3$. The complexing action of citric acid on alkaline-earth cations does not become appreciable in elution until a pH of about five is reached (*13*, *15*). The pK values for citric acid (*14*) are pK = 3.1, pK_2 = 4.8, and pK_3 = 6.4.

EXPERIMENT

In the experiment described here, 12.8-day Ba^{140} and its 40-hr. La^{140} daughter are initially in transient radioactive equilibrium. An ion-exchange resin column is used to separate the daughter from the parent. The separated La^{140} fraction is observed to decay with its characteristic 40-hr. half-life. The growth of the 40-hr. La^{140} as observed by γ counting in the purified barium fraction expressed by equation (1), is observed. After equilibrium has been reached the γ activity of the barium fraction (40-hr.La^{140}) is described by equation (2). Extrapolation of the decay curve to the time of separation gives A_d^0. The separation of La^{+3} from Ba^{+2} is made by eluting the cations absorbed on the resin bed with a solution of 5 per cent (0.24 M) citric acid brought to a pH of~4 with concentrated NH_4OH. The La^{+3}, strongly complexed by the citrate, is removed from the column while Ba^{+2} remains. When no La^{+3} remains on the resin, the pH of the influent solution may be raised to~6 and the Ba^{+2} rapidly removed.

Elution curves for a nearly carrier-free activity removed slowly from an ion-exchange column have the shape of a normal Gaussian curve (*2*, *17*). The position of the maximum of activity is related to the distribution constant K_d and the half-width of the curve is related to K_d and the effective number of perfect plates in the column (*17*).

Materials

(1) *The resin column* is glass tubing of 10-mm. inside diameter and 25-cm. length. The column is fitted with a rubber stopper which holds a stopcock. A plug of glass wool above the stopper will retain a column of cation resin 10 cm. in length, in suitable state.[5] The 100-mesh resin, poured in as a slurry, is tapped to remove all air bubbles and to avoid channeling. The uniform bed that is obtained insures constant flow during the experiment. Dropping rate is adjusted to about 4 ml. per minute.

(2) *Two 5 per cent citric acid solutions* are prepared; one is brought up to pH 3.8 and the other to pH 6.0 with concentrated NH_4OH. Ten-ml. formalin may be added to each solution as a preservative. The column is conditioned for the separation by running through the eluting solution of pH 3.8 until the effluent pH is that of the influent.

(3) *The tracer* needed is a relatively concentrated stock solution of Ba^{140}–La^{140} with less than 5 mg. of natural barium carrier. For γ counting of 10-ml. aliquots with a Geiger-Mueller counter (γ counting effi-

[3] For a related experiment using radiotracers and ion-exchange technique under equilibrium conditions, see (*13*).

[4] See also Ketelle and Boyd (*16*), and Tompkins and Mayer (*17*).

[5] For preparation of the resin (Dowex-50), see (*2*) or (*13*).

ciency about 1.5 per cent) of geometric acceptance about 20 per cent, approximately two microcuries (μc) of Ba^{140} is required. Substantially less activity is required if a 5–10-ml. sample is counted in a recessed (Na,Tl)I scintillation counter, since its γ counting efficiency and geometric acceptance are much higher.

(4) *Laboratory equipment* includes 24 18×150-mm. test tubes and No. 1 solid rubber stoppers. Twenty-four 10-ml. aliquots are removed during the elution as described below. The collected samples are quickly stoppered and counted. An aliquot of the stock solution, diluted to 10 ml. and sealed in a test tube, is used as a volume and activity standard.

(5) *The counting apparatus* should be selected to take advantage of the energetic gamma radiation emitted by La^{140}. A lead or wood shield may be built to hold the 18×150-mm. test tubes at a reproducible geometry adjacent to a standard end-window counter, an Eck and Krebs counter tube, or a scintillation counter. The β particles of the Ba^{140} and La^{140} are absorbed in the solution and glass and essentially only the γ rays emitted by La^{140} are measured.

Procedure

A small aliquot of the known stock solution of Ba^{140}–La^{140}, containing suitable activity, is absorbed on the column. The lanthanum fraction is then eluted with the citrate solution of pH 3.8. Ten 10-ml. fractions are collected in the test tubes, the sample volume being measured by comparison with the standard. The dropping rate (about 4 ml. per minute) is slow enough so that no eluate is lost on changing tubes. Each 10-ml. sample is quickly stoppered and counted. After the tenth fraction, the flow is stopped until the second eluting solution of pH 6.0 is used. Fourteen 10-ml. samples are required to remove the barium. The 24 samples corresponding to a total eluate of 240 ml. can be collected in 55 minutes.

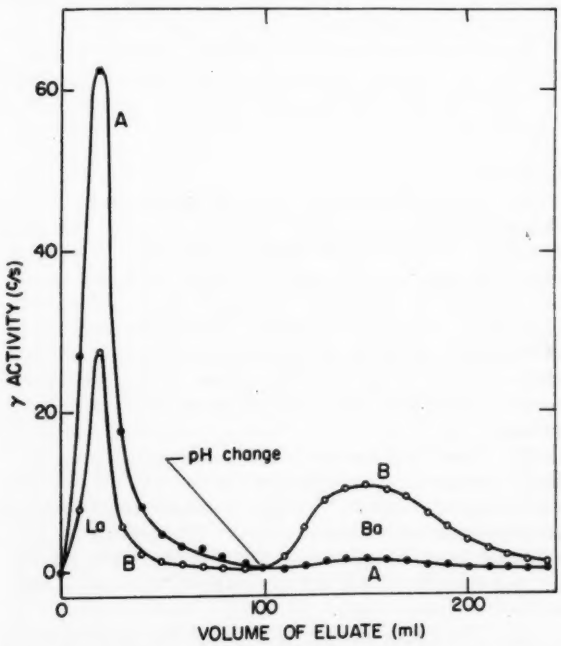

Figure 1. Curve for the Elution of Lanthanum (La^{140}) and Barium (Ba^{140}) from Dowex-50 by Five Per Cent Citrate Buffer (pH 3.8, then 6.0)

Curve *A*, γ counting immediately after sample collection; curve *B*, γ counting of same samples after three days (La^{140} activity grown from Ba^{140}).

The gamma activity found in each sample is plotted as a function of volume of eluate. The initial curve will give the Gaussian elution curve for the lanthanum fraction. No significant activity is apparent for the barium fraction since the γ-emitting La^{140} has been removed and the Ba^{140} γ radiations are not sufficiently intense to be detected. After transient radioactive equilibrium has been approached the samples may be recounted to show the barium elution curve. The peak aliquots of the lanthanum fraction can be measured regularly to show its 40-hr. half-life, and the peak aliquots of the barium fraction can be measured over the same time interval to show the growth of the lanthanum in accord with equation (1).

Discussion

The degree of separation can be determined from inspection of the elution curve. The area under the La^{140} curve taken before its decay represents the total activity in the original stock solution taken, while the area under the Ba^{140} curve some days later is proportional to the total activity of the barium. The overlapping then represents the contamination of each element fraction by the other. The activity ratio of 40-hr. La^{140} to 12.8-day Ba^{140} in transient equilibrium when extrapolated to the time of separation is:

$$\frac{\lambda_d}{\lambda_d - \lambda_p} = 1.15$$

Thus, the Ba^{140} activity can be determined even though only the gamma radiation of the La^{140} is being measured. Both the La^{140} and Ba^{140} total activities are extrapolated back to the time of separation and for perfect separation the ratio of these two should be 1.15. If the counting is done after seven days rather than at transient equilibrium, the theoretical ratio of La^{140}/Ba^{140} is 1.08.

Typical curves obtained during an experiment are shown in Figures 1 and 2. Figure 1 shows the elution curve *A* measured during the experiment, and *B* the same samples measured three days later. The area under the lanthanum maximum of curve *A*, obtained by adding the activity values observed in the ten 10-ml. aliquots, represents La^{140}. The area under the Ba^{140} curve measured seven days later corresponds to the total activity of the Ba^{140} when it is divided by 1.08. This number, corrected for seven days' decay of Ba^{140}, represents Ba_0^{140}. Figure 2 shows the decay of a lanthanum fraction and the experimentally observed growth of lanthanum in the barium samples. The solid lines in Figure 2 represent theoretical curves.

With a stock solution of Ba^{140}–La^{140} having a gamma activity of 72 c./s./ml. determined by the standard, the

results obtained from an experiment absorbing 2 ml. on the column are given in the table.

Assuming the recovery of Ba^{140} complete, the recovery of the separated La^{140} in the lanthanum fraction is

$$\frac{(1.06 \pm 0.06)100}{1.15} = (92.4 \pm 5.2)\%$$

EXTENSION TO GENETIC STUDY: La^{140} RESERVOIR

The experiment outlined above (*18*) provides for the separation of lanthanum from barium by elution of cation-exchange resin with suitable citrate buffer. In principle, separate tracers could be used for the two elements, and the two fractions could be identified by their separate Gaussian-shaped elution curves (like curve *B* of Figure 1), with perhaps a precipitation made with carrier to distinguish the lanthanum peak from the barium peak if the separate characterization of the radiations is too difficult (as with β radiations). Suitable qualitative tests include separation of $La(OH)_3$ with NH_4OH; separation of $La_2Ox_3 \cdot 10H_2O$ with oxalate ion Ox; separation (*12*) of $BaCl_2 \cdot H_2O$ with concentrated HCl–ether; separation (*11*) of $Ba(NO_3)_2$ with fuming HNO_3; or careful separation of $BaSO_4$ with H_2SO_4. It is less desirable to use a tracer for one element and appreciable amount of carrier for the other, with precipitation-identification of the latter, because of interference in column behavior by loading of the carrier (*2, 3*).

In the discussion section, advantage was taken of the genetic relations existing between 12.8-day Ba^{140} and 40-hr.La^{140} to compute the elution efficiency, which should be 100 per cent for lanthanum. It is more useful pedagogically to consider an extension of the experiment whereby the half-life of the parent species Ba^{140} can be determined (*18*) by successive elutions at equal intervals (say 7 days) of the daughter activity. This technique is known colloquially as "milking."

Equation (1) has the property that for equal times of growth t, the daughter activity A_d^o, totalized for the whole lanthanum fraction and extrapolated to time of elution, is proportional to A_p at the time of elution. Thus the half-life of Ba^{140} can be established from a plot of the logarithm of successive A_d^o values against time of successive elutions if the column is operated at pH 3.8 where only lanthanum is removed. The barium band moves very slowly at this pH value.

If a column is set up for lanthanum extraction at weekly intervals, various members of the class could make the successive elutions, and pool their results for analysis and reporting. If a sample time is missed or if the data are taken at irregular elution intervals, an obvious more sophisticated application of equation (1) must be used to obtain the half-life of the Ba^{140}.

If the ion-exchange column is set up as described and used only for lanthanum elution (*18*), it is seen that it acts as a reservoir for La^{140} extraction, but the capacity of the reservoir decays with the 12.8-day half-life of Ba^{140} rather than the 40-hr. half-life of separated La^{140}. Such usage is a convenience in radiochemical work.

It would be a useful senior research problem to establish a pH value for citrate buffer that would lead to effective one-step (batch) extraction of La^{140} from a reasonable mass of cation-exchange resin containing Ba^{140}, without significant contamination by Ba^{140}. By virtue of the convenient half-lives, one batch of resin can be used throughout the school term for successive experiments spaced at weekly intervals. In addition, γ counting made on the leach solution the day the experiment is made will measure essentially only La^{140}, whereas counting the sample one week later will measure 0.74 of the original activity of Ba^{140} plus 0.054 of the original La^{140}. A measurement two weeks after the extraction gives 0.53 of the original Ba^{140} activity with no contamination from initial La^{140} in excess of transient equilibrium. The same type of experiment could be used to explore the complexes of lanthanum and barium.

Results of a Typical Experiment

Total La_0^{140} = (129.6 ± 3.9) c./s. (2.0 ml.)
La^{140} counted in Ba^{140} after 7 days = (90.7 ± 2.7) c./s.
Ba^{140} after 7 days = $\frac{90.7}{1.08}$ = (84.0 ± 2.7) c./s.
Total Ba_0^{140} = (122.5 ± 3.7) c./s.
$\frac{La_0^{140}}{Ba_0^{140}} = \frac{129.6 \pm 3.9}{122.5 \pm 3.7} = 1.06 \pm 0.06$

ACKNOWLEDGMENT

The authors gratefully acknowledge the advice and

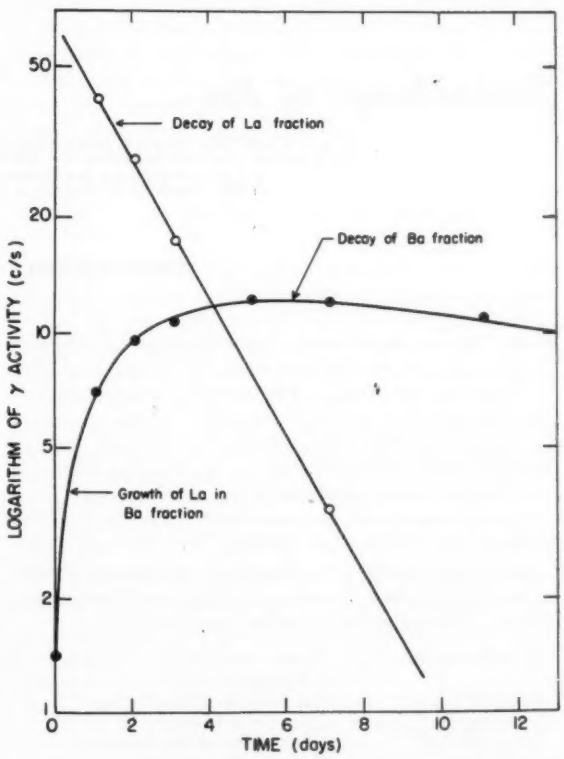

Figure 2. Experimental γ Growth and Decay Curves for Radiochemically Pure Samples of 40-hr. La^{140} and 12.8-day Ba^{140}

assistance of Dr. Jack A. Marinsky of Ionics, Inc., and of Dr. Jack Schubert of the Argonne National Laboratory. This work was supported in part by the U. S. Atomic Energy Commission through the M. I. T. Laboratory for Nuclear Science.

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Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

JOINT MEETING WITH A.A.A.S.

THE Pacific Southwest Association of Chemistry Teachers met at the University of California, Berkeley, on December 29, 1954. The meeting was planned to coincide with the annual convention of the American Association for the Advancement of Science, held at Berkeley from December 26 to 31, so that members could attend other programs of interest to them.

The business meeting was called to order at 2:30 P.M. in Room 217, Chemistry Building, Dr. Howard Benninghof, City College of San Francisco, presiding; Mother Agnes Schmit, San Francisco College for Women, secretary. The following members were present:

Alice Marie, Sister	Mount St. Mary's College, Los Angeles
Ballou, G. A.	San Francisco State College
Benedict, H. C.	Chico State College
Benninghof, H.	City College of San Francisco
Coad, Peter	College of San Mateo
Edwards, Bentley	University of California, Berkeley
Frantz, H. W.	Pasadena City College
Furst, Arthur	Stanford Medical School
Holmes, Jerome K.	Hartnell College
Houk, A. L.	Calif. Polytech. College, San Luis Obispo
Kallo, J. H.	Fresno State College
Jonte, J. H.	College of the Pacific
Lofgren, Norman	Chico State College
Martin, Raymond M.	Sacramento Junior College
Mooney, W. T.	El Camino College
Phillips, Valerie	City College of San Francisco
Rakestraw, Norris W.	Scripps Institution of Oceanography
Rankin, L. H.	College of San Mateo
Redeker, H. E.	College of San Mateo
Reiber, H. G.	University of California, Davis
Robertson, G. Ross	University of California, Los Angeles
Schmit, Mother Agnes	San Francisco College for Women
Schwenk, J. Rae	Sacramento Junior College
Smith, Art	Humboldt State College
Womack, E. B.	Fresno State College

It was considered unnecessary to read the minutes of the last meeting, held at San Luis Obispo, January 8 and 9, 1954, as they had already been published in

THIS JOURNAL, May, 1954. The treasurer's report was read by Miss Valerie Phillips in the absence of Sister Agnes Ann, Treasurer:

TREASURER'S REPORT

Income	
Balance, January, 1954	$330.48
Amount received during 1954 through membership dues	240.00
Refunds from J. CHEM. EDUC.	2.50
Total	572.98
Expenditures	
Expenses in transfer of treasury	$ 7.42
Expenses of San Luis Obispo Meeting (outstanding from 1953)	41.85
Secretarial materials (outstanding from 1953)	18.07
JOURNAL subscriptions for each member	182.50
Refunds made to members	6.00
Total	255.84
Bills still outstanding against account	
For secretarial materials for 1954, probably	$ 20.00
For transfer of funds to new treasurer	5.00
Income	$572.98
Expenditures	255.84
Balance in treasury, Dec. 29	317.14

SISTER AGNES ANN
Treasurer

Dr. Benninghof then announced the results of the election for officers for 1955: Dr. Norris W. Rakestraw, Scripps Institution of Oceanography and JOURNAL OF CHEMICAL EDUCATION, President; Dr. Ralph A. Barmore, Pasadena City College, Secretary; and Dr. J. Gordon Sewell, Sierra College, Treasurer. The Vice-presidents of the Association are: Dr. Manfred Mueller, City College of San Francisco, Chairman of Northern Section, and Dr. Harper Frantz, Pasadena City College, Chairman of Southern Section.

The chair then opened for discussion the problem of bringing the Northern and Southern Sections closer together for more effective accomplishment at our joint meetings. Dr. Frantz responded by suggesting that we have the meetings more centrally located and announced that a cordial invitation had been extended to the association by Santa Barbara College to meet there on Saturday, February 12. He outlined a tentative program for the meeting, prepared by Dr. Norman Kharasch, Chairman-elect of the Southern Section. He announced also the meeting at UCLA for the Southern Section on Saturday, March 12, and invited all members to attend this meeting. Dr. Rakestraw expressed the view that he too had been hoping that we could make the Association a more unified and stronger organization and that he intended, as the new president, to work on this. He was of the opinion that the problem was bound up with the increase of membership and that we should continue to grow; then perhaps break up into more divisions so as to have not only a Northern and Southern, but also a Central Section.

The growth of membership brought up two new questions: (1) that of dues, and (2) that of inviting high-school teachers who are interested in chemistry to join the association. Dr. Womack expressed the view that many more high-school teachers would join the association if they were not required to subscribe to the JOURNAL OF CHEMICAL EDUCATION at the same time. A discussion followed over the variance in local dues required by the Northern Section ($0.50 per year) and the Southern Section ($1.00 per year). Dr. Frantz reminded the group that the amount of dues had been fixed by the constitution and that it could not be decided upon by the individual sections. Dr. Rakestraw did not think the dues should be stipulated as an established amount in the constitution. He moved that the constitution be amended to delete from it the exact amount of the dues and place the determination of the amount of the dues in the hands of the executive committee. The motion was seconded. Action on the motion was deferred until all the members could be notified.

Dr. Womack then proposed that the Northern Section should encourage high-school teachers interested in chemistry to join the association. He noted that the Southern Section includes high-school teachers in large numbers. Dr. Rakestraw agreed and added that one of the good features of the association was that its meetings from the beginning had furnished a place where college and high-school teachers of chemistry could meet on common ground to their mutual benefit. Dr. Benninghof then called for a motion on this subject. Dr. Art Smith, Humboldt State College, moved:

Resolved, that high-school teachers interested in chemistry be encouraged to join the Pacific Southwest Association of Chemistry Teachers.

The motion was seconded and carried. As there was no further business, the meeting adjourned at 3:00 P.M.

At 4:00 P.M. members who were interested attended the A.A.A.S. general symposium: Science and Society III: Science in Human Thought and Action, at the Wheeler Auditorium. The program follows:

(1) "The role of the sciences in education," Joel H. Hildebrand, emeritus professor of chemistry, University of California.
(2) "Science and international cooperation," Bart J. Bok, professor of astronomy, Harvard University.
(3) "Logics and the human nervous system," John von Neumann, Institute for Advanced Study, Princeton, New Jersey.

At 6:30 P.M. the group met for dinner at the Men's Faculty Club, where the guest speaker was Dr. Arthur Furst, associate professor of medicinal chemistry, Stanford University. His subject was "The chemist's approach to the cancer problem."

AGNES SCHMIT
Secretary

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Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

TRENDS IN CHEMICAL EDUCATION[1]

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Pennsylvania State University,
University Park, Pennsylvania

As TEACHERS of general chemistry, in schools, colleges, and universities, we need to pause once in a while to consider some of our general problems. Accordingly, several topics or problems of rather general interest to all chemistry teachers will be discussed briefly under the title "Trends in chemical education."

CHEMICAL NOMENCLATURE

The general problem of chemical nomenclature deserves the attention of the chemistry teacher, who is all too familiar with the difficulties of the student in this matter. Scott[2] presented a rather thorough study of this problem about ten years ago, at a symposium on nomenclature sponsored by the Division of Chemical Education.

The revised system of nomenclature prepared by the International Union of Chemistry[3] has met with rather conservative acceptance by authors of textbooks in general chemistry. Of three new textbooks or revisions of textbooks published this year, only one[4] appears to make use of this system. One of the well known and widely used introductory texts[5] revised in 1950 was, apparently, the first to make use of the new system. An important feature of this system, it will be recalled, is that the oxidation numbers (or valence numbers) of the positive ions of compounds are expressed by Roman numerals. This scheme is, of course, particularly useful in the case of compounds of copper, iron, etc. The old terms cuprous, cupric, ferrous, ferric are replaced by the more specific and, it is to be hoped, more workable system of numbers, *e. g.*, copper(I) oxide, copper(II) oxide, iron(II) sulfate iron(III) sulfate. In naming the oxides of nitrogen, to take another example, one uses the terms dinitrogen monoxide for N_2O, nitrogen oxide for NO, dinitrogen tetroxide for N_2O_4, etc. The compound $K_4Fe(CN)_6$ is called tetrapotassium hexacyanoferrate, and the compound $K_3Fe(CN)_6$ is called tripotassium hexacyanoferrate. To indicate the oxidation numbers (valence) of iron, one could add the numbers II and III to these names, *e. g.*, for $K_4Fe(CN)_6$, tetrapotassium hexacyanoferrate(II).

With regard to terminology, one still finds in the newer textbooks some terms which are incorrectly used, *e. g.*, "molecular weight" of ionic substances (NaCl, $CuSO_4 \cdot 5H_2O$, etc.) which do not exist as discrete molecules. In such cases, the term "formula weight" appears to have a more direct application. Another familiar and time-honored label is "NH_4OH." A brief review[6] of work on the ammonia-water system indicates that there is little justification for the use of this label.

Many antiquated terms still appear in our chemistry textbooks and literature, *e. g.*, blue vitriol, quick lime, burned lime, hard water, soft water, and perhaps many other items which convey either an ambiguous or an erroneous chemical meaning to the student.

ORGANIZATION OF TOPICS

Segregation of subject matter into distinct major categories, *e. g.*, Descriptive Chemistry, Theories and Principles, Chemical Calculations, etc., has been done by some authors.[7,8,9,10]

The relative merit of this method of presentation is,

[1] Presented at the Sixteenth Summer Conference of the NEACT, University of Massachusetts, Amherst, Mass., August 19, 1954.

[2] SCOTT, J. B., "The need for reform in chemical nomenclature," *Chem. Revs.*, **32**, 73 (1953).

[3] JORISSEN, W. P., ET AL., "Rules for naming inorganic compounds," *J. Am. Chem. Soc.*, **63**, 889 (1941).

[4] ROCHOW-WILSON, "General Chemistry," John Wiley & Sons, Inc., New York, 1954.

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[6] DAVIS, J. B., "Ammonia and 'ammonium hydroxide,'" J. CHEM. EDUC., **30**, 511 (1953).

[7] LATIMER AND HILDEBRAND, "Reference Book of Inorganic Chemistry," Macmillan Company, New York, 1951.

[8] HILDEBRAND AND POWELL, "Principles of Chemistry," Macmillan Company, New York, 1952.

[9] MCCUTCHEON AND SELTZ, "General Chemistry," D. Van Nostrand Company.

[10] PARKS AND STEINBACH, "Systematic College Chemistry," Blakiston, New York, 1952.

of course, a debatable point. A fundamental fact to be kept in mind is that, in the development of chemistry as a science, experimental facts, generalizations, and technical applications have come into the picture in a rather closely related sequence or pattern.

With reference to the historical development, one is reminded of the problem: In what order should the periodic system and atomic structure be presented?

There are teachers who hold that since the periodic system was worked out many years before we knew anything about the structure of atoms, the periodic system should be presented before atomic structure. Other teachers argue just as strongly that, because the work on atomic structure is so fundamental, it should be presented first. Perhaps the teacher should let the students vote on this question.

CARBON CHEMISTRY VERSUS QUALITATIVE ANALYSIS

Without minimizing the importance of the inorganic chemical industries, it is important to note the very extensive growth of the organic chemical industry. It is estimated[11] that the organic chemical industry is expanding at a rate of four times that of all U. S. industry; that "in 20 years more than half the nation's organic chemicals production will be in products unknown today"; that in the next ten years, 100,000 new jobs will be created in the organic chemical field.

It seems probable that many electrical and mechanical engineers will be employed in plants which manufacture organic chemicals, and that some instruction in organic chemistry will be not only helpful but essential in their work. When only one year's work in general chemistry is included in the curricula in electrical and mechanical engineering as is often the case, it is obvious that the course in general chemistry might well include more work in organic chemistry.

Whether or not the organic chemistry is more difficult for freshmen to learn can best be answered by those who teach such courses. Experience in general chemistry at our own institution has been hitherto limited to the usual two weeks on hydrocarbons and carbohydrates. We find that the students express unusual interest in this work and do as well or better than they do on some of the topics in inorganic chemistry. A survey of several recent texts containing approximately 500 pages and essentially of the "nonmajor" type, shows an increasing coverage of organic chemistry (up to 40 per cent of the total content) (Table 1). In line with this trend, our course in general chemistry for students in agriculture, engineering, home economics, and physical education at the Pennsylvania State University has been revised to include more work on organic chemistry. This work replaces the brief and empirical presentation of qualitative analysis (6 weeks) in the second semester. It is recognized, of course, that qualitative analysis has held a time-honored place in the general chemistry course in many institutions. In our regular one-year course in general chemistry (10 credits) for majors in chemistry, chemical engineering, premedical, and other related curricula, qualitative analysis of the semimicro type is included and will be retained as a part of the second semester's work. For the students in these fields the theory and the techniques of qualitative analysis are generally regarded as having great educational and training values as a preparation for scientific work. For the students in general agriculture, engineering, home economics, etc., many of whom take only a brief one-year course in chemistry, it is a debatable point as to whether the work on elementary organic chemistry may not be of more interest and value than the brief study of "ionic separations" or qualitative analysis.

This plan is, of course, an experimental one. It is hoped that the systematic relationships as well as the practical importance of organic chemistry will stimulate the interest and contribute to the intellectual growth of our students.

LABORATORY VERSUS TEXTBOOK

One of the difficult problems in the teaching of elementary chemistry is the divided emphasis, or shall we say dual viewpoint in connection with the use of a textbook and a laboratory manual. Every teacher of general chemistry probably will concede that the most direct learning of chemistry comes, or should come, from the laboratory experience of the student. In our teaching, however, we tend to place more emphasis on the textbook material. In all too many cases, the student gets the impression that the experimental work is largely a matter of illustration or confirmation of the material

[11] WAGNER, CAREY, Pres. Synthetic Organic Chemical Manufacturer's Assoc., *Chem. Eng. News*, **32**, 697 (1954).

TABLE 1

Comparison of Textbooks in General Chemistry (Relative Emphasis on Carbon Chemistry)

Author	*Title*	*Total pages*	*Pages on carbon chemistry*	*% of text carbon chemistry*
Damerell	"A Course in College Chemistry"	531	216	40.6
Watt and Hatch	"Science of Chemistry"	538	188	35.0
Garrett, Haskins, and Sisler	"Essentials of Chemistry"	525	147	31.0
Richardson and Scarlett	"Brief College Chemistry"	353	45	12.7
Briscoe	"College Chemistry"	548	68	12.4
King and Caldwell	"College Chemistry"	568	59	10.4
Smith-Ehret	"Introductory College Chemistry"	500	48	9.6
Cavelti	"Introductory General Chemistry"	408	38	9.3

TABLE 2
The Master of Education Degree Conferred at P.S.U. in Science and Other Fields (5-Yr. Period 1949–53)

	Total degrees conferred	*Chemistry and phys. sci.*	*Biological sciences*	*Education*	*All other fields*[a]
1949	200	0	2	113	85
1950	281	0	4	270	7
1951	330	1	5	206	118
1952	342	4	7	215	116
1953	301	2	3	210	86
	1454	7	21	1014	412
		0.5%	1.4%		

[a] All other fields: agr. ed., art ed., business ed., home ec. ed., ind. ed., music ed., phys. ed., speech ed., languages, social studies.

presented in the textbook. To a certain degree this aspect of the laboratory work may be a desirable one, but the thoughtful and perhaps less ambitious student can rightfully say, "What's the use of doing the experimental work when we know the answers because they are all in the book?" Some of the laboratory manuals of the workbook type which include certain exercises involving only the tabulation of facts or data from the textbook, may be especially conducive to this point of view.

To correct this undesirable tendency or practice, some writers have prepared texts which make the individual experimental work the focal point of the course.[12,13]

The first-named publication presents the basic concepts as an integral part of the laboratory work. The student is expected to find related descriptive material in the larger texts which are made available for reference in the laboratory. The writer, unfortunately, has had no experience with this type of teaching and would like to be in position to try it. Another phase of this problem, and closely related to it, is the question: Should the laboratory work precede or follow the lecture and recitation work? A plan which the writer follows (in college general chemistry) involves the sequence; (1) lecture, (2) laboratory, (3) recitation. The ideal situation would be to have a flexible schedule, so that a given topic or unit may be studied in whatever way seems most effective, *i. e.*, by formal lecture demonstration, individual experimental work, or class discussion—with all of these activities in charge of the same teacher.

In at least one textbook in qualitative analysis[14] the authors have attempted to correlate the lectures with the laboratory work on certain topics.

SCIENCE TEACHERS

The trend in the supply of science teachers deserves careful study. The curves[15] showing the numbers of graduates prepared to teach mathematics, general science, biology, chemistry, and physics for the years 1949–53 show an increase from 1949 to 1950 and a very alarming decrease from 1950 to 1953. Some factors responsible for the current shortage of science teachers are: higher salaries offered in technical fields, military drafts and enlistments, and shifting of science teachers to administrative positions. Anticipating future needs in terms of increasing school population, the conference report makes the following statement:[16] "Already the need for new science teachers . . . exceeds 7000 per year and will approach 10,000 per year in the immediate future. Since the total annual pool of potential science teachers is now about 5000, a serious shortage seems inevitable unless drastic actions are taken at once."

To implement this action, the conference report makes seven recommendations, two of which are stated as follows: "4. Liberal-arts and teachers colleges concerned about the quality of instruction in secondary schools immediately begin, in cooperation with professional scientific societies and associations, vigorous recruitment campaigns for secondary-school teacher candidates especially in science and mathematics"; "6. School administrators concentrate responsibility for science teaching among a minimum number of qualified teachers."

Of the increasing number of secondary-school teachers earning master's degrees, it is of interest to know what proportion do their graduate work in chemistry and other sciences. Data from the records of one state university for the five-year period from 1949 to 1953 are summarized in Tables 2 and 3. It is to be noted that of the 1454 individuals who took the M.Ed. degree, only 28 or about two per cent did their major work in the sciences (only seven in chemistry).

Assuming that many of the 1014 students whose major work was in education are currently in administrative work or will eventually enter this field, it appears that their science background is not sufficient as a basis for sound judgment in administering science courses.

The degree of Master of Science (M.S.) was conferred upon 1156 individuals at the same institution (Table 3). During the same five-year period, 111 or 9.6 per cent of these individuals did their major work in chemistry, 74 or 6.4 per cent in physics, and 122 or 10.5 per cent

[12] STONE AND MCCULLOUGH, "Experiments, Theory, and Problems in General Chemistry," McGraw-Hill Book Co., 1953.
[13] GORDON, "College Chemistry," World Book Co., 1926.
[14] FALES AND KENNY, "Inorganic Qualitative Analysis: Semi-Micro Techniques with Estimation of Concentration," Appleton-Century-Crofts, Inc., New York, 1953.
[15] "Critical Years Ahead in Science Teaching," Report of Conference on Nation-wide Problems of Science Teaching in the Secondary Schools, Harvard University, July-August, 1953, p. 12.
[16] *Ibid.*, p. 19.

in biochemistry or biological sciences. In round numbers, about 25 per cent majored in the physical and biological sciences and 75 per cent majored in the various applied or technical fields, *e. g.*, agriculture, engineering, home economics, mineral industries, etc. Presumably very few, if any, of the 25 per cent who majored in the physical and biological sciences did enough work in the field of education to legally qualify them as teachers of science in the public schools. Again, this "M.S. group" cannot be regarded as a potential group of science teachers even though they are well qualified as to their training in the sciences.

Some of the factors which have brought about this discouraging situation are, of course, well known: relatively lower salaries paid to science teachers, as compared to salaries paid to principals and superintendents, insufficient credits in undergraduate science courses, as prerequisites for the graduate courses in science; greater amount of time necessary for the laboratory science, especially in the summer sessions.

In the liberal-arts colleges, the situation is presumably not as discouraging as in the case of the larger technical institutions. The writer is of the opinion that a considerable number of students, especially women, are being well trained as science teachers in the arts colleges and in some of the state teacher's colleges.

TABLE 3

The Master of Science Degree Conferred at P.S.U. in Science and Other Fields (5-yr. Period 1949–53)

	Total degrees conferred	*Chemistry*	*Physics*	*Biochem. and biol. sci.*	*All other fields*[a]
1949	235	30	11	18	176
1950	234	25	17	30	162
1951	253	25	22	27	179
1952	240	19	9	30	182
1953	194	12	15	17	150
	1156	111	74	122	849
		9.6%	6.4%	10.5%	

[a] All other fields: agr., eng., home ec., mineral industries, etc.

To the Editor:

Dr. Meldrum's paper on the teaching of equivalent weights (THIS JOURNAL, **32,** 48 (1955)) is testimonial to the difficulty of presenting this topic to students. Many practicing teachers may have murmured "How true!" when they read the conclusion that "teaching of equivalents is a situation which is, for the most part, vague and baffling to the student."

Has not the time come to bring up for debate the question of the advisability of teaching the equivalent concept? I realize that anyone who would suggest the possibility that the equivalent concept is not indispensable is certainly spitting into a very high wind.

Students do seem to gain without too much difficulty a working concept of such concrete material as atoms, molecules, electrons, and molecular weights. But the nebulous equivalent never seems quite to gel.

For what it is worth, may I venture to suggest that the factitious normality system be completely scrapped. Problems in volumetric analysis can be solved more readily by using a millimole analysis. The millimole method has in its favor the emphasis on the equation of the reaction actually taking place in the titration vessel. To me this makes good teaching sense.

SHIRLEY W. GADDIS

SOUTHEAST MISSOURI STATE COLLEGE
CAPE GIRARDEAU, MISSOURI

To the Editor:

On page 668 of the December, 1954, issue of THIS JOURNAL, A. Viswanathan and S. Azmatullah mention the behavior of soap bubbles blown by a person who has inhaled hydrogen. They mention the danger of breathing hydrogen containing poisonous impurities, but they neglect the more serious danger of explosion. Several people have been killed while demonstrating the effect of hydrogen on the pitch of spoken words.

People who wish to blow light bubbles should stick to helium. Otherwise they are in danger from any accumulation of static electricity—especially during the winter conditions the authors (in Madras) do not need to worry about.

RICHARD M. NOYES

COLUMBIA UNIVERSITY
NEW YORK, N. Y.

ELEMENTS OF FOOD ENGINEERING. VOLUMES 2 AND 3

Milton E. Parker, Consulting Food Engineer, *Ellery H. Harvey* formerly Professor of Food Engineering, and *E. S. Stateler,* formerly Professional Lecturer in Food Engineering, Illinois Institute of Technology. Reinhold Publishing Corp., New York, 1954. Vol. 2: vi + 360 pp. Illustrated. 16 × 23.5 cm. $8.50. Vol. 3: v + 241 pp. Illustrated. 16 × 23.5 cm. $6.75.

THESE two volumes develop the details of unit operations applied to food processing as outlined in the first volume of this series. Section 1 deals with assembly of raw materials under Materials Handling and Separating. The preparation of raw materials is divided in Section 2 into Cleaning, Separating, Disintegrating, and Pumping. The conversion of raw materials, Section 3, involves Mixing, Heat Exchange—Heating Applications—Refrigerating Applications, Evaporating and Distilling, Dehydration and Drying, and Controlling. The treatment of final products, Section 4, is divided into Coating, Decorating and Forming, Packaging—Materials—Methods.

The treatment is essentially descriptive. The authors have assembled a valuable mass of information concerning the application of unit operations to specific food processes. The choice of equipment is made easier by discussion of the advantages and disadvantages each offers for particular jobs. The approach used is apt to prove disappointing to the engineer though it should be useful to one newly introduced to the food industry. Study of unit operations as developed in these volumes will serve to acquaint the food technologist with the existence of problems the solution of which must be sought in more thorough engineering treatment.

As a text for college students this series of three volumes should furnish a good introduction to engineering and technical problems which the graduate will encounter upon entering the food processing industry. A few minor errors were noted but are not of material consequence. The illustrations are profuse and add a great deal to the value of text.

For the smaller food manufacturer without specially trained technical staff, this presentation of the elements of unit operations as applied in the industry can serve well to orient him to his needs for further engineering guidance.

JOHN H. NAIR

THOMAS J. LIPTON, INC.
HOBOKEN, NEW JERSEY

ARTIFICIAL FIBRES

R. W. Moncrieff. Second edition. John Wiley & Sons, Inc., New York, 1954. xii + 455 pp. 144 figs. 14.5 × 22 cm. $6.

THE word "artificial" as applied to fibers has a different connotation in England than in America, thus explaining its use. There is a stigma associated with the word "artificial" in the United States. A title more consonant with scientific progress and, at the same time, having wider appeal would be desirable.

The original edition has been expanded to cover the developments in the field of man-made fibers in recent years and the author has tried to delineate the salient properties of each fiber. Most of the additional information relates to new man-made fibers, the new methods of dyeing required, and the great strides made by the staple versions, especially in blending with other fibers. A chapter dealing with the economic and social aspects of man-made fibers is helpful from the standpoint of perspective. A list of fibers, comprising approximately sixty types, marketed under trade names, is given, while separate chapters discuss the individual fibers under the caption Trade Names.

The reviewer believes that a précis, organizing the data into (1) vinyl and acrylic fibers, (2) polyamide fibers, and (3) polyester fibers, etc., and discussing the proprietary fibers under these general headings would reduce redundancies and improve clarity.

Since it is difficult to obtain the desired technological information pertaining to new synthetic fibers before the manufacturing process and the properties of the fiber have been standardized and the patent structure established, errors are prone to occur in the data presented. Some of these could have been corrected by submission of the manuscript to the respective fiber producers. Evidence of this is found in the statement, "It is evident 'X-51' has been spun from the melt. . . ." The statement, "The felting process of wool is entirely due to the scale system. . . ," is not in accord with the opinion of authorities on this subject.

One understands the author's defense of wool in the statements: "Most likely, in fifty years time, it will still be true to say there is nothing like wool," and "It will probably be a long time indeed before an artificial fiber which is a good match for wool can be made." Wool is an important factor in the textile economy of Britain, but these statements would seem to be more germane to the wool industry than to scientists doing research on fibers made from synthetic polymers.

The new edition will be found useful by a wide range of readers as a source, within the covers of one book, of information on man-made fibers. A need exists for a book containing the general scope of information presented; but it is hoped that the next edition will present a more authoritative and balanced account of the new fibers and that the author's viewpoint will be entirely objective.

J. B. QUIG

E. I. DU PONT DE NEMOURS & COMPANY
WILMINGTON, DELAWARE

THE FUNDAMENTALS OF COLLEGE CHEMISTRY

G. Brooks King, Professor of Chemistry, The State College of Washington, and *William E. Caldwell,* Professor of Chemistry and Chemical Engineering, Oregon State College. Second edition. American Book Company, New York, 1954. viii + 589 pp. 55 figs. 37 tables. 14 × 22 cm. $4.50.

A REVIEW of the first edition is to be found in THIS JOURNAL (26, 571 (1949)). This new edition is improved by various additions to the text. The electronic configuration of atoms is described in greater detail, and differences in properties between elements are explained in terms of atomic size and structure. A brief discussion of complex salts, several pages more on radioactivity and nuclear changes, and an additional page on electrode potentials are further examples of additions to the text. The solution of gas-law problems by substitution in formulas is still encouraged, but in the new edition examples are also given showing how the solution may be obtained by common sense, without recourse to formulas. This is a step in the right direction. The

term "hydronium ion" and symbol H_3O^+, used in the first edition, have been replaced by "hydrogen ion" and H^+ with a resulting gain in consistency and clarity.

The most obvious change is the addition of approximately 50 per cent more "exercises" and "references." The exercises now represent a greater range of difficulty and include some interesting and challenging problems. Answers are given for some of the numerical problems. Production, price, and use data in the tables and text have been brought up to date, as has also the periodic table. A long-form periodic table has been added and a new figure shows the relative sizes of atoms and ions. The index is more effectively organized and contains about 20 per cent more entries than the previous edition. The purpose and structure of this edition are the same as in the first edition; the changes increase its usefulness and improve its clarity without changing its character.

WALTER B. KEIGHTON

SWARTHMORE COLLEGE
SWARTHMORE, PENNSYLVANIA

• THE TECHNOLOGY OF SOLVENTS AND PLASTICIZERS

Arthur K. Doolittle, Assistant Director of Research, Carbide and Carbon Chemicals Company. John Wiley & Sons, Inc., New York, 1954. xv + 1056 pp. Many figs. and tables. 14.5 × 22.5 cm. $18.50.

SOME feeling of insecurity comes to the student chemist in his occasional glimpses of the large amount of unfamiliar, empirical technology upon which successful industrial enterprises may be based. Much of this technology cannot be treated in the student's academic career for any of several reasons: (*a*) its clear relationship to basic principles may not yet be evident, (*b*) appreciation of its significance may require firsthand knowledge of its manner of application to practical purposes, (*c*) the time required to master its complex mass of detail may not be commensurate with its value to the majority of students, and (*d*) the various essential parts of a given technology have usually not been brought together in up-to-date, accessible form with expert integration into a unit.

The last-named of these chasms between the student and the technology of industrial solvents has been solidly bridged by Dr. Doolittle. He has brought together in a single volume a veritable treasure of facts, principles, and lore relating to the industrial uses of solvents and plasticizers up to recent times. It is readily apparent to the reader of his book that Dr. Doolittle has enjoyed an active, inquisitive, and successful career in the field which is his subject.

The book is directed primarily to the practicing chemist or technician, rather than to the student. The technician concerned with formulating products containing solvents will know the intended meaning of such terms as "alkyd" (p. 48), "blushing" (p. 98), "fluxing" (p. 125), "calendering" and "press polishing" (p. 868); the average student, and perhaps his professor, will not. Even though the meanings of such terms must be deduced from the context or sought in other references, the book is easy to read and should bring a rich return to the tyro whose curiosity leads him into its pages.

Eighty per cent of the volume is concerned with industrial solvents, and their treatment is comprehensive. The vast literature on the theory of solutions seems to have been condensed and highlighted with good judgment, with the needs and desires of the practical man in mind. Extensive tables and charts are included which will serve as ready sources of data on vapor pressures and other characteristic physical properties of a host of solvents. Data are collected together on the solubility of typical resins in common solvents. A table of azeotropic mixtures and their properties and composition embraces those most likely to be encountered in commercial practice. The discussion of the industrial uses of solvents is superb, and interest is added by appropriate synopses of the historical background of current practices.

To say that only 20 per cent of the volume is devoted to plasticizers carries an inaccurate implication, for much of the discussion of solvents applies equally well to those specialized solvents which are called plasticizers. In the author's words, "The characteristic that differentiates plasticizers from solvents is volatility."

One cannot avoid the conclusion, however, that plasticizers have not been given the thorough, thoughtful treatment accorded the more conventional solvents. The relative emphasis may be in fair agreement with the relative commercial importance of the two fields. However, much more could be said about the standards by which various plasticizers are chosen for various applications, about combinations of plasticizers and why they are so frequently used together rather than singly, and about performance properties and test methods for their evaluation. It is a ticklish matter for an author to editorialize about competitive proprietary products, but the formulator who consults this book for help in choosing plasticizers may well be disappointed. The brief, occasional mention of polymeric plasticizers is hardly commensurate with their growing commercial importance.

Nevertheless, for its intended purposes, this volume genuinely deserves to be described by the word "monumental." It is at once a textbook, a handbook, and an encyclopedia which should never be farther away than arm's reach for the technical man whose work involves solvents, diluents, and extenders.

ELLINGTON M. BEAVERS

ROHM AND HAAS COMPANY
PHILADELPHIA, PENNSYLVANIA

• STARCH AND ITS DERIVATIVES. VOLUMES I AND II

J. A. Radley, Chemical Consultant. Third edition. John Wiley & Sons, Inc., New York, 1954. Vol. I: xi + 510 pp. Vol. II: xi + 465 pp. 15 × 22.5 cm. $10 per volume.

STARCH chemistry, like other carbohydrate fields, has made tremendous strides forward in recent years. This progress in fundamental chemistry and technology has been the basis for a number of authoritative publications of which the work from Great Britain here being reviewed is one of the best.

Many of the topics covered in Radley's volumes are the same as those included in Kerr's "Chemistry and Industry of Starch," an American book of somewhat similar character. One even notes, with some surprise, that the authors of certain sections are the same in both works. On the whole, however, the present volumes tend to supplement and extend rather than to duplicate the literature already available. The extensive lists of references which accompany most chapters are indicative of the scholarship of the work and afford an added value for the user.

Volume I is divided into two parts of which the first is devoted to The Structure and Reactions of Starch. Most of the chapters of this part are contributed by such prominent workers in the field as S. Peat, L. Hough, J. K. N. Jones, T. J. Schoch, R. L. Whistler, G. V. Caesar, R. M. Hixon, B. Brimhall, and E. G. Degering. One of these chapters, "The starch fractions," by T. J. Schoch is the most complete discussion of this important topic available and is supported by 437 references with an extensive cross index of subjects.

The chapter, "The waxy cereals and starches which stain red with iodine," by R. M. Hixon and B. Brimhall, also constitutes a thorough discussion of a topic not adequately reviewed elsewhere.

Part II of Volume I is concerned with Amylases and Their Action on Starch, and is an exhaustively documented discussion of general features and nomenclature, preparation of enzymes used in the starch industry, the action of α- and β- amylases on starch, the kinetics of amylase action, and methods of determining the activity of amylase preparations.

Volume II is divided into three parts covering The Manufac-

ture, The Industrial Applications, and The Examination and Analysis of Starch and Starch Products. Several chapters are contributed by specialists including R. W. Kerr ("Corn starch manufacture"), C. W. Bice and W. F. Geddes ("The role of starch in bread staling"), C. C. Kessler and W. G. Bechtel ("Physical methods of characterizing starch"), and C. Paine ("Notes on the significance of patent references").

The chapters contributed by the author, J. A. Radley, show a wealth of experience with starch and its industrial applications. During the preparation of this review the reviewer had occasion to look up certain topics of a practical nature with which he was concerned and found much information of great value in its specific details.

"Starch and Its Derivatives" can be highly recommended not only to those interested in the finer problems of starch chemistry but also to those who work with starch in industry.

IRWIN B. DOUGLASS

UNIVERSITY OF MAINE
ORONO, MAINE

● LEHRBUCH DER GESAMTEN CHEMIE

F. L. Breusch, **Professor of Chemistry at the University of Istanbul. Second edition. Springer Verlag, Berlin, 1954. vi + 426 pp. 85 figs. 42 tables. 17 × 25 cm. DM 29.70.**

IT IS always interesting to look over textbooks used in other countries, for new ideas. This book, designed for general science and premedical students, is not comparable to any book now on the American market. Ninety pages of general physical chemistry, 130 pages of descriptive inorganic chemistry organized rigidly element by element, and 220 pages of organic chemistry follow one another in a very thoroughly ordered array. The style is more encyclopedic than continuous, and expository than experimental. The flavor throughout is strongly biochemical. Many of the illustrations are novel, but I doubt that the book as a whole could have much impact toward guiding authors in worthy innovations for the American market.

J. A. CAMPBELL

OBERLIN COLLEGE
OBERLIN, OHIO

● THE INFRA-RED SPECTRA OF COMPLEX MOLECULES

L. J. Bellamy, **Principal Scientific Officer, Ministry of Supply, England. John Wiley & Sons, Inc., New York, 1954. xvii + 323 pp. 30 figs. 22 tables. 14.5 × 23 cm. $7.**

PREVIOUSLY there have been only two sources of information on the empirical correlation of infrared spectra with molecular structure: various "correlation charts," and the original literature. This volume puts under one cover much of the previously scattered information, and will be welcomed by everyone interested in the measurement and understanding of infrared spectra. Its scope is strictly limited. There are no discussions of experimental technique, though the influence of physical state and solvent is mentioned where important; nor is the theory of molecular vibrations treated, though the results are sometimes used as an aid in assigning observed bands. Other topics, such as hydrogen bonding and rotational isomerism, are treated briefly from the correlation standpoint. The basis for all correlations is a large number of observed spectra, some unpublished from the author's laboratory, and others from the more than 800 literature references listed; the literature was covered to about 1953. The 30 figures are spectra of some typical compounds.

The book is devoted almost exclusively to organic compounds; six pages describe the spectra of inorganic ions. Of the remainder about 80 per cent covers the spectra of organic compounds containing no element other than carbon, hydrogen, oxygen, and nitrogen. Additional sections cover, in varying degrees of detail, organic compounds of phosphorus, silicon, sulfur, and the halogens. Bands for correlation are broadly classified by the "linkages" involved: C—C and C—H, C—O and O—H, C—N and N—H, and those involving other elements.

Five pages of correlation charts containing 180 entries are given first. The remainder of the book contains some 70 more correlations, with a detailed discussion of each. Usually included are the approximate number of different molecules on which the correlation is based, frequencies in some specific compounds, and differences in band positions, either random or caused by effects such as conjugation, an electronegative substituent, ring strain, etc. Also mentioned are approximate intensity and, in a few classes, the possibility of one's using intensity to determine the number of given groups in the molecule. For some compounds, where there is disagreement on a correlation in the literature, the author quotes all sides rather fully before stating his position.

Some may object to the exclusive use of frequency ($cm.^{-1}$) instead of wavelength, even though a short table of reciprocals is appended; however, the reviewer believes that this shows the author's foresight. Errors seem to be very infrequent, and mostly typographical; but the author apparently prefers the cyclic model for diazomethane. The indexing is adequate for the location of a specific individual compound or a class of compounds. However, starting with an unknown substance and its spectrum one would refer to the correlation charts for the possible classes of compounds, and then to these classes in the text. The printing is generally good, but the type in the correlation charts is too small for reading comfort.

The author is to be commended for a good, much needed book. It will find frequent use in many research and control laboratories. While it is clearly not intended as a textbook, it might be suitable as a supplement or a source of material in a course of instruction.

DAVID F. EGGERS, JR.

UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

● CAREERS AND OPPORTUNITIES IN SCIENCE

Philip Pollack. **Second edition. E. P. Dutton & Co., Inc., New York, 1954. 243 pp. Illustrated. 14 × 21 cm. $3.75.**

THIS is a book which should be not only on the shelf of every vocational guidance counselor, but also in the school library in a place readily accessible to the secondary-school student, for in an interesting and simple manner it tells of the many opportunities open to the interested person who has "the price of admission."

After a general overview of the new fields that have resulted from recent scientific discoveries, Mr. Pollack writes a challenging chapter on the Price of Admission. Here he speaks realistically of the qualifications demanded by a career in science, listing and discussing such qualities as intelligence, accuracy in observation, visual and scientific imagination, general accuracy, alertness, perseverance, patience, and compatibility with people in general.

There follow nine chapters in which the opportunities open in the fields of chemistry, physics, meteorology, agriculture, conservation, medical research, geology, and a number of other branches of science are discussed. Included in the descriptions are thumbnail sketches of men and women who have carved out careers in the field under consideration, as well as fascinating accounts of the scientific discoveries which have made such careers possible.

There is a fine chapter on the place of women in the picture, a chapter which, while showing that women are now employed in practically every scientific field, does not minimize the handicaps under which they must work. Mr. Pollack points out the fact that they must usually be satisfied with a lower salary schedule, and that their acceptance is necessarily limited by the employer's fear that they will not work permanently.

Fittingly, the book closes with a look ahead, in a chapter en-

titled Careers for Tomorrow. While some of the possibilities which are suggested may seem fantastic, others are quite within the realm of probability, and the vigorous imagination needs no further stimulus in picturing the future which "extends a welcome and an unprecedented opportunity to the science-trained young man or young woman of to-day."

DOROTHY W. GIFFORD

LINCOLN SCHOOL
PROVIDENCE, RHODE ISLAND

• THE PHYSICS OF EXPERIMENTAL METHOD

H. J. J. Braddick, Senior Lecturer, University of Manchester. John Wiley & Sons, Inc., New York, 1954. xx + 404 pp. Illustrated. 14 × 22.5 cm. $7.

IT IS a commonplace that the data of physical science are largely obtained from carefully controlled experiments. It is therefore all the more surprising that modern books on general experimental techniques in physics as distinct from the usual laboratory instruction manuals are very rare. The volume under review fills the gap in admirable fashion. To quote the author, the purpose is "to direct attention to those branches of physics which are important in the planning and execution of experiments in physical research." Considerable attention is paid to the principles of physical experiment, presently available resources, and the fundamental limitations of contemporary techniques. The book is thus by no means merely a collection of useful laboratory arts and recipes.

Among the unusual features in a book of this kind is the thorough treatment of errors of measurement, the discussion of general principles of the design of apparatus to achieve the maximum efficiency in measurement, a detailed presentation of the properties of materials used in apparatus construction, and a good chapter on the natural limits of measurement ("noise" considerations, etc.). Special fields of research like electronics, optics, and nuclear physics, come in for adequate attention. Here the author evidently consulted his own interests to a considerable extent, realizing the impossibility of doing justice to all branches. Thus, acoustics is conspicuous by its absence, though the acoustician will find some useful ideas in the electronic techniques discussed.

The volume is written in a clear and straightforward style with the needs of the average advanced student in mind. It should appeal, indeed, to the wider circle of all those who use physical equipment in their investigations. The references could have been made more useful by employing the initials of the names of the authorities cited. A more complete index would also render the book more valuable for reference.

R. B. LINDSAY

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

• PRINCIPLES OF BIOCHEMISTRY

Abraham White, Albert Einstein College of Medicine, *Philip Handler,* Duke University School of Medicine, *Emil L. Smith,* University of Utah College of Medicine, and *DeWitt Stettern, Jr.,* National Institutes of Health. McGraw-Hill Book Company, Inc., New York, 1954. xii + 1117 pp. 135 figs. 100 tables. 16 × 23 cm. $15.

THE growing number of comprehensive textbooks in biochemistry receives an important addition as four authorities combine their abilities to produce this new publication. Each author is a well known contributor to fundamental research, and three are currently teachers. Their great individual resources take on added significance in this teamwork.

The book follows a neatly logical development with its 50 chapters falling into parts as follows: I, Chemical Composition of Cells; II, Catalysis; III, Metabolism; IV, Body Fluids; V, Biochemistry of Specialized Tissues; VI, Biochemistry of Endocrine Glands; VII, Nutrition. Generally biochemistry texts have devoted special sections, usually at the beginning, to a discussion of the physical-chemical principles to be used in the presentation of material. This book shows a refreshing and useful departure from this procedure by presenting the necessary discussion of physical chemistry within the framework of the text. The writers say: "It has been the experience of the authors that the interest of the student is much greater when particular chemical concepts are illustrated with a biological or biochemical principle close at hand."

About one-third of "Principles of Biochemistry" is taken up with enzyme systems and intermediary metabolism. Since these represent by far the currently most productive facet of the discipline, the emphasis is correct. It is also fortunate that, of the well written text, these two sections containing the most difficult and important material are the best handled.

The book will find its widest application in medical schools. The field of biochemistry is so broad and ever-growing that the best one can hope to do in a course for medical students is to permit them a "brush" with the subject. "Principles of Biochemistry" is an excellent text for this purpose, though it would be foolhardy to expect that any preclinical student will be able, in the time allotted, to comprehend and retain all of this or any other 1100 pages of solid information.

ELIOT F. BEACH

METROPOLITAN LIFE INSURANCE COMPANY
NEW YORK, N. Y.

• LEHRBUCH DER ORGANISCHEN CHEMIE. BAND I, ERSTE HÄLFTE: KOHLENWASSERSTOFFE, HALOGEN UND SAUERSTOFF VERBINDUNGEN

Friedrich Klages, Professor of Organic Chemistry, University of Munich. Walter de Gruyter & Co., Berlin, 1952. xv + 531 pp. 17.5 × 24.5 cm. DM 68.

THIS is the first unit of a substantial work under four covers, others being Volume I, Part 2, nitrogen, sulfur, etc., compounds; Volume II, history and modern theory; and finally Volume III, special topics—dyes, carbohydrates, etc.

Volume I, Part 1, already in print, opens with a 57-page chapter on fundamental principles. The presence here of such items as hydrolysis of esters, organic free radicals, carbonium ions, etc., before the first paragraph on systematic study of methane, ethane, etc., leads one to infer that the German user of the book will have already studied elementary organic chemistry in the fashion of a first-class European secondary school.

Advanced modern organic theory is left for a distinct compartment of the work, Volume II. Aside from the two theoretical portions of the "Lehrbuch," the principal part of the publication is a well written exposition of standard, systematic organic chemistry. Unlike classical German treatises, however, in this work aliphatic and aromatic chemistry are unified, chapter by chapter. The author considers this union to be essential in a modern treatment of the subject, but many American teachers will not agree with this premise. While aliphatic and aromatic material may have been fused, modern theory and systematic organic chemistry are still largely separate.

Segregation of theory from the systematic material provokes the comment that current organic texts, English and American as well as the "Lehrbuch," are in a primitive stage, suggestive of the inorganic textbook of about 1900. The author of that early era would leave a short space in the middle of his factual presentation, and take time off for a chapter dealing with new ideas on "ions," credited to one Arrhenius. This done, he returned to the main job, straight inorganic chemistry, and finished the book.

Following, in one sense, the inorganic pattern, one may regard

the "Lehrbuch" as a transition stage in organic textbooks, advanced only a little beyond the 1900 plan with respect to connection of theory with facts. In other words, the next few years will witness in organic textbooks a wholly new interrelation and unification of modern theory with the great body of detailed information for which German scholars deserve so large a share of the credit. Such unification cannot come at once, in the face of widespread presumption that the modern study of reaction mechanism is an "advanced" topic which the youth studies *after* he has mastered the fundamentals of organic chemistry proper. But the new school of physical-organic chemists does not agree with such presumption, and it is very likely that these modernists will have their way. It should also be remembered that physical organic chemistry is no longer merely the use of physical instruments on organic material for deciphering structure.

A few minor criticisms come to light: Continued use of elongated hexagons to represent the benzene ring; use of line enclosures in structural equations—for example, surrounding H and OH symbols, leading students to infer that the reaction in question occurs because hydrogen is seeking hydroxyl—and finally, unnecessary complication in numbering of volumes. The reviewer wishes to register vigorous disapproval of the old-time German publishers' habit, appearing once again, of numbering the units of a multivolume series in subnumbers (of uncertain tally) as well as main numbers, to the confusion of booksellers, librarians, and readers. There seems to be no good reason why the "Lehrbuch" should not be numbered simply as Volumes I, II, III, and IV.

These items are, of course, of minor import. By contrast, the splendid typography far outweighs the shortcomings. Skilful use of boldface type and variation in size of ordinary roman type are highly commendable. The "Lehrbuch" should serve for a decade or two as a worthy follower of Meyer and Jacobson, and of von Richter, as an excellent main reference book in the private library of the young German scientist. We wonder, however, where the poor fellow is going to get the money to pay for it at three cents a page.

G. ROSS ROBERTSON

University of California
Los Angeles, California

● MODERN ASPECTS OF pH

James Small, Professor of Botany, Queen's University, Belfast D. Van Nostrand Co., Inc., New York, 1954. xi + 247 pp. 30 figs. 26 tables. 14.5 × 22.5 cm. $5.

This book should appeal mainly to botanists and soil scientists, and it seems unfortunate that the title should not so indicate. The inclusion of a subheading, "with special reference to plants and soils," may not be adequate to attract all those interested. Those in the field probably will know the author's two previous books: "Hydrogen Ion Concentration in Plant Cells and Tissues," (1929) and "pH and Plants" (1946). In this new publication, the table of contents and casual examination show that more than three-quarters of the subject matter is devoted to a review and discussion of published research on pH measurements of plant materials and soils. The early chapters give a historical review of the pH scale, the significance of the concept of activities of ions as compared to concentrations, and a discussion of buffer systems in general.

To a chemist the relation between activity and concentration of ions is not new, as this is adequately covered in the common physical chemistry texts. A chemist would also regret the dearth of equations in the book, as they are so valuable, and, of course, are widely used in discussing problems involving equilibria. Typical of this is the explanation (pp. 24–5) of the effect of adding "alkali" to 0.1 *N* acetic acid, and of the resulting buffer solution. Again, the discussion (p. 117) relative to $CaCO_3$ curves could be more fundamental with the aid of a few simple equations showing the equilibria, and the precipitation phenomenon then accounted for on the basis of the usual solubility-product rules.

These examples—and others could probably be cited—merely illustrate the opinion that the book is written for the plant or soil scientist rather than the general chemist. The review of published research in the two fields, supported by the selected bibliography, seems excellent and worth while. Those acquainted with the author's previous works will certainly wish to read this one as well.

The format, as well as the arrangement, is satisfactory. The American reader may be somewhat surprised that many of the figures and tables appear to have been reproduced from hand-printed originals, but this in no way detracts from their value.

H. G. REIBER

University of California
Davis, California

● BENTLEY'S TEXT-BOOK OF PHARMACEUTICS

Revised by *Harold Davis, M. W. Partridge,* and *C. L. Sargent.* Sixth edition. Williams & Wilkins Co., Baltimore, 1954. xiii + 1078 pp. 302 figs. 14.5 × 22.5 cm. $10.

A sixth edition of "Bentley's Text-Book of Pharmaceutics" became a necessity when a new British Pharmacopoeia and changes of the syllabus of the examination for registration as a pharmacist rendered certain parts of the previous (1949) edition obsolete.

The American reader is obviously inclined at first to consider such a book as this of little interest, assuming that it probably deals at length with pharmaceutical practices alien to ourselves and of value only to members of this profession in Great Britain. A closer look, however, reveals that the 1078 pages of this book contain a wealth of information which can be useful and of interest to pharmacists, chemists, and biologists anywhere.

Part I gives (in 22 pages) a short history of the British Pharmacopoeia and an account of the origin and production of the International Pharmacopoeia. Part II (143 pages) describes the general principles involved in pharmaceutical operations, but the emphasis is on principles and not on pharmaceuticals. For example, there is a discussion of solubility curves, distribution coefficients, X-ray analysis of crystals (showing the structure of benzylpenicillin as example), freeze drying, osmotic pressure and isotonic solutions, viscosity, surface tension, various types of chromatography, ion exchange, and enzymes. There follows Part III, devoted to pharmaceutical processes (237 pages), which extends all the way from diagrams of vacuum pumps to homogenizers and refrigeration plants. Part IV (143 pages) deals with dispensing, Part V (211 pages) is devoted to microbiology and presents a study of bacteria and molds, including methods for the preparation of vaccines and sera. Finally there are Parts VI and VII, dealing with surgical dressings (35 pages) and pharmaceutical preparations (239 pages), respectively. An appendix gives tables of doses.

The book as a whole is very well written and has a large number of excellent illustrations. It is undoubtedly essential for the practicing pharmacist, but I believe it will also interest a much larger group of chemists who like to get reliable information on the interplay of the many specialties which participate in the "drug business."

OTTO SCHALES

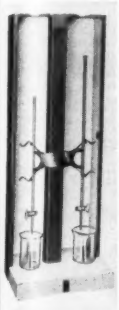
Alton Ochsner Medical Foundation
New Orleans, Louisiana

◆ ◆ ◆

Out of the Editor's Basket

Illuminated Titration Stand

Precision Scientific Company has redesigned the Senior "Titra-Lite," a titration stand which provides soft, evenly diffused "daylight" illumination for both the titration burettes and flasks. The redesigned stand features the use of the "Full-View" Burette Clamp, which keeps burette markings fully visible; rubber-covered friction grips exert just the right force against the burettes to hold them securely without danger of breaking.



The "Titra-Lite" eliminates eye-strain, is ideal for close work, providing even light diffusion without harsh shadows or blinding bright spots, and without light "spill" into the laboratory. Accuracy is promoted—there is no "false color" diffraction—and time is saved, since more distinct color transitions prevent running over end points, eliminate extra titrating. Side ports facilitate recharging of burettes during continuous titrating, making the Senior "Titra-Lite" ideal for process control operation.

Literature is available on request from Precision Scientific Company, 3737 W. Cortland Street, Chicago 47, Illinois.

Demineralizer

A dual-type demineralizing unit—designated as Model R-M-8—has just been announced by the Penfield Manufacturing Co., Inc. of Meriden, Connecticut. This new mono-column demineralizer can be used with a single bed of mixed cation and anion resins, or as a two-bed system with separate cation and anion resin beds in the single column.

With either system, the unit produces up to 10 GPH of demineralized water with as little as 10 grains sodium chlorides (expressed as $CaCO_3$). If desired the unit is capable of removing silica and CO_2 as well, through the use of special resins. Regeneration is simple and fast with costs of regenerant chemicals only about 10¢. Complete information on the R-M-8 may be secured by writing Mr. Edward H. Clohessy, Gen. M'gr., Penfield Manufacturing Co., Inc., 19 High School Avenue, Meriden, Connecticut.

Flame Photometer

A new Model 146 Flame Photometer, styled for maximum ease of operation and performance, has been announced by The Perkin-Elmer Corporation, Norwalk, Connecticut. The improved instrument incorporates several features to permit simple and precise read-out of data, enabling a relatively inexperienced operator to turn out accurate determinations over long periods with minimum fatigue.

Each control has been designed and positioned on a molded fiberglass panel for maximum convenience. Data are read out on counters instead of vernier dials.

Model 146 may be operated either as a direct reading instrument or as an internal standard ratio instrument. The time required for analysis is less than one minute per element with an accuracy of ±1%. Better than ±1% is possible with more time and care. A sample size of two to five cc. is sufficient for an analysis.

Analyses may be made in solution on sodium, lithium, potassium, magnesium, calcium, strontium, barium, chromium, manganese.

Unesco Seeks to Bring the Benefits of Science to All Countries

Unesco's program for 1955–56 in the field of Natural Sciences, will deal mainly with the application of atomic energy for peaceful purposes; studies of oceans and deserts in order to harness their potential for food and power; and the dispatch of technical aid missions to individual nations which have recently started programs of industrialization.

It is often forgotten in the Western part of the world that the benefits of science—whether they be such simple things as running water, a gas stove, or a household gadget—can make a valuable contribution to economic and social progress.

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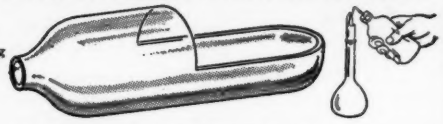

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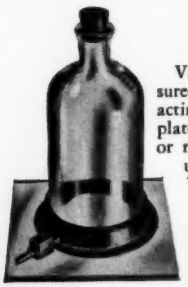

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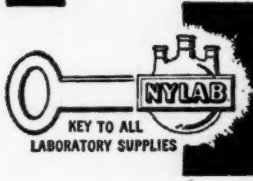

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Since economic progress is dependent upon a local supply of technicians and artisans whose education has been soundly based on science subjects; since, furthermore, it depends upon experimentation and research which is carried out in universities and laboratories, seventeen specialist missions have been authorized for dispatch during the next two years, ranging all the way from science teaching in secondary schools to the creation of science faculties in universities. This work will eventually enable the countries concerned to have their own trained technicians and research workers.

To help overcome the lack of scientific equipment both for teaching purposes and for workshop use, a portfolio of workshop designs was published in 1954 to enable underdeveloped countries to construct some 80 pieces of basic scientific equipment from local materials. In 1955 it is planned to set up a demonstration work room in science teaching at Unesco headquarters for the briefing of experts proceeding on missions and for the information of teachers. It will contain tools and materials for making simple equipment, a collection of visual aids in science teaching, and a reference library of textbooks on this subject.

In addition, it should be mentioned that work on four major regional scientific documentation centers in Mexico, Yugoslavia, Egypt, and India (and one minor one in Uruguay) will be completed by the end of 1955. Work at these centers, which are basic to technical and industrial research, was begun some years ago: the one in Mexico City was in fact taken over by the government during 1954. This is a practical example of the value of scientific technical aid in a Member State.

To help bring science home to the people of underdeveloped countries a program of traveling exhibits which started touring in 1948 will be continued in the future program and local science clubs and associations of science writers will be encouraged.

At the present time Unesco has three traveling exhibits on the road covering such subjects as physics, astronomy, instruments employed to measure the universe, and synthetic materials in use today. These exhibits have already been seen in 26 countries; the one on synthetic materials, which has recently been in the Middle East, reached Montevideo early in November and had its Latin American opening in conjunction with the eighth Session of the General Conference.

Turning back now to the other specific activities—oceans, deserts, and atomic energy—the Unesco program may be briefly summarized as follows:

First, the oceans. Over 25 per cent of the world's food comes from salt (and fresh) water, but science knows that this percentage could be greatly increased through study of the ocean bed and the habits of fish in general. For example, many nutritious salts, existing deep down in the sea, only come near the surface when ocean currents behave in a certain way: if, therefore, a means could be found for "upwelling" these salts, the consequent increase in fish supply might be considerable.

Second, the deserts. Since arid conditions occur on all continents and cover more than one-fourth of the land surface of the earth, Unesco has focused research on desert problems since 1948 in order to make those areas more productive and thus improve the living conditions of the inhabitants.

Under the direction of a 9-member committee, called "The Advisory Committee on Arid Zone Research," Unesco seeks to coordinate research undertaken by all Member States in this field. Emphasis is placed each year on one important subject, such as the supply of underground water, plant life, or wind and solar energy.

Within the next few months a handbook of research data on arid zones will be published to guide those who are active in their development. Using this data as a basis Unesco will, over the next two years, carry out surveys in two specific desert areas and produce plans for their actual development. The work of putting these plans into practice would be a matter for the Member States concerned which could possibly obtain specialist aid from United Nations technical assistance funds.

Third, atomic energy. Unesco's work in this sphere will form part of the general plan for the development of atomic energy for peaceful purposes, initiated by President Eisenhower, and now being worked out by the United Nations. For example, Unesco will help in the preparation, from the scientific standpoint, of working documents for the International Conference on this subject which is to be held during 1955. Together with WHO, Unesco will make a particular contribution to the study of the effects of radio-active substances in general even though this energy is to be used for peaceful purposes. Such studies will concern the effect of contamination on water, air, soil, and daily food.

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GENERAL BIOCHEMISTRY

by WILLIAM H. PETERSON & FRANK M. STRONG, University of Wisconsin

At last, here is a basic text which achieves an excellent balance between descriptive chemical aspects and the presentation of the dynamic aspects of plant, animal and microbial metabolism. Important features include: 1) chapters on Hormones and Energetics give much new and technical information, 2) the newest developments in photosynthesis and nitrogen fixation are reviewed extensively, 3) selected problems and questions follow each chapter, 4) documentation has been stressed, 5) there are many halftones, charts, tables, full-color photos, 6) the book is written in a simple, direct style and all technical terms are clearly defined when they first appear.

Among 1954 adoptions: Cornell University, Carnegie Institute of Technology, De Paul University, New York University, Lehigh University, University of California (Berkeley).

6″ x 9″ • 469 pages • Published 1953

COLLEGE CHEMISTRY

by PAUL R. FREY, Colorado Agricultural & Mechanical College

If any text can be considered the standard work in its field, this one can. More than 200 schools have adopted it. Praise ranges from "...emphasizes what I have considered for a long time to be among the prime essentials of a college textbook" to "...a distinct contribution" and "...judicious intermingling of descriptive and theoretical chemistry throughout."

The book earns these comments because, 1) it is logically organized. Inert gases are presented first, then the author ranges back across the periodic table all the while developing the *concept-building* theme. 2) where possible, subject matter has been divided into qualitative and quantitive aspects for flexibility. 3) many solved problems are included, together with lists of carefully graded exercises and problems. 4) there are almost 300 illustrations, suggested readings, list of film library teaching aids, complete chemical reference library, vapor pressure and log tables, conversion factors for weights & measures.

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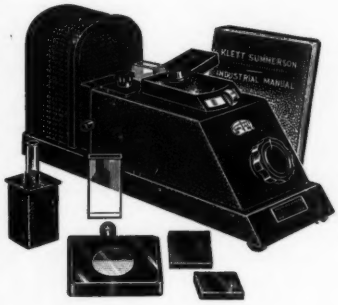

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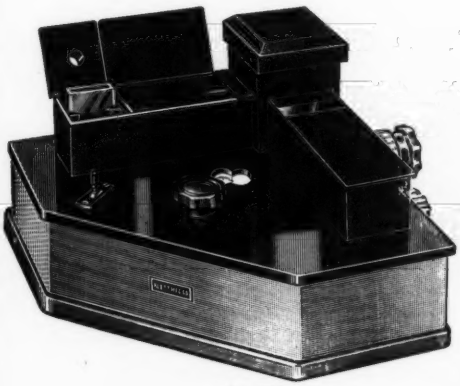

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It should go without saying that all Unesco's work in the scientific field is based on the universality of science—on the fact that science knows no boundaries and that all scientists are eager to share their knowledge with their counterparts in other countries for the benefit of man's conditions. The results of their research and discoveries are the life blood of Unesco's own scientific activities.

For this reason Unesco maintains a world center of scientific liaison at its headquarters in Paris and regional science offices on five continents. It also strengthens relations between scientists on a worldwise basis by convening conferences and expert meetings and, in particular, by granting subventions and contracts to the many voluntary scientific organizations which have been created over the past 50 years.

Finally, it may be mentioned that as the benefits of science are spread to all countries, so there is hope that living standards will be improved: this fact, in its turn, has a market value, since it is known that people with a reasonable standard of living are good customers.

Vinyl-based Protective Coating

A new hot-spray-applied vinyl-based protective coating that builds a film thickness in two coats equal to five coats of cold spray vinyl coatings, has just been announced by The U. S. Stoneware Co., Akron, Ohio.

The new coating—Tygon ATD—combines vinyl and other plastic resins to form a high solids content viscous material that reverts to a liquid form on the application of heat, thus avoiding the use of excessive amounts of solvents to achieve spraying consistency.

Tygon ATD is brought to a temperature of approximately 160°F. in a standard paint heater. An air pressure of 20 lb. forces the heated paint to the spray gun where it is atomized by 50 lb. of air. As the hot paint leaves the spray gun most of the incorporated solvents are evaporated and a thick, high solids content film is deposited on the target. Since but little solvent remains in the film, drying is remarkably quick.

Tygon ATD Hot Spray Paint is resistant to the attack of most commercially used acids and alkalies, as well as to alcohols, water, and oils. It is, however, attacked by aromatic hydro-carbons, ketones and esters. Full details may be obtained by writing Mr. G. W. Fine, The U. S. Stoneware Co., Akron 9, Ohio.

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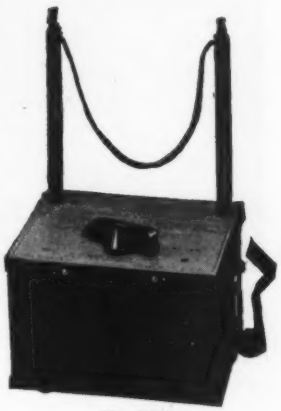

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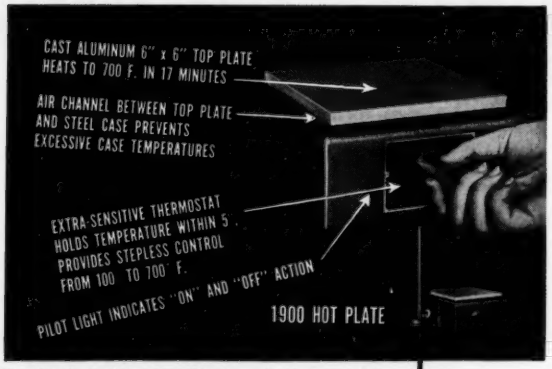
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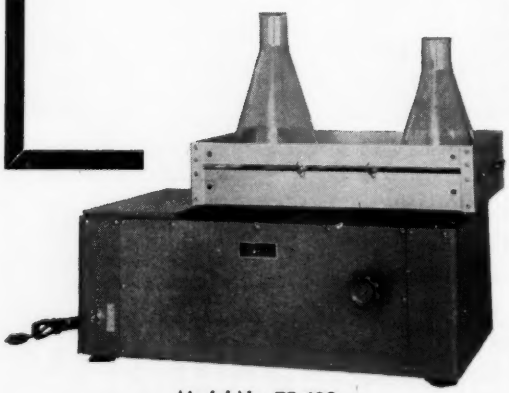

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$C_{19}H_{21}NO_4$

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$C_{15}H_{14}O_6 \cdot 4H_2O$

Corydaline MP 230–40°
$C_{22}H_{27}NO_4$

Diacetone Galactose
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2-Hydroxyfluorene MP 171°
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$C_6H_{15}NO$

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C_5H_7N

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For this all-inclusive working Rotameter Catalog, please request Bulletin No. 115, Brooks Rotameter Company, Lansdale, Pennsylvania.

● A new 4-page two-color bulletin describes the new Lapp "Microflo" Pulsafeeder Pump. A new piston-diaphragm pump, it is described as operating against pressures up to 1000 psig and has a maximum flow rate of 2400 ml. per hour. "Microflo" features include *no stuffing box, packing, or running seal* in contact with liquid being pumped. Complete description, specifications, and prices are included in the bulletin which is identified as Bulletin No. 500 and will be sent on request by Lapp Insulator Co., Inc., Process Equipment Div., 10 Gilbert Street, LeRoy, New York.

● Bulletin 1800 C on Consolidated Engineering Corporations' Type 21-103C mass spectrometer is now available. It emphasizes the economy, speed, versatility, accuracy range, and sensitivity of this in

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150	69	4.0c

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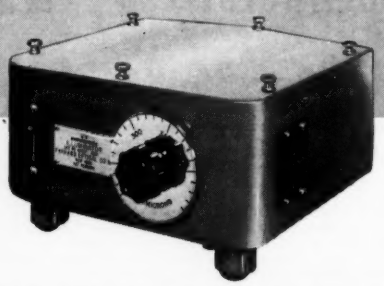

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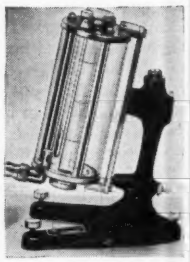

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Write for Bulletin HV-303, which gives complete details

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strument. Information is also given on the operations, the components, the applications, and service. Contact the Public Relations Department at 300 North Sierra Madre Villa, Pasadena 15, California, for a copy.

● A comprehensive chart showing more than 120 organic syntheses based on orthonitrochlorobenzene, (ONCB), is available from Monsanto Chemical Company's Organic Chemicals Division, St. Louis 4, Missouri.

The 35-by-44-inch wall chart presents in sequential form the chemical methods for the synthesis of ONCB compounds according to three general classifications: Ring substitutions, chloro reactions, and nitro reactions.

In addition, the chart contains a literature summary of potential uses for 19 of the more important ONCB derivatives. The company also has reissued technical data sheets on three ONCB derivatives not shown in the chart: 2-mercaptobenzoxazole, *o*-nitrobenzenesulfenyl chloride, and beta-(*o*-chloroanilino) propionitrile. These products are available in laboratory quantities.

Material for the chart was compiled from published journal and patent literature by scientists of the Monsanto laboratories.

MISCELLANY

★The possibility of radioactive contamination of public water supplies from the use of nuclear weapons or from improper disposal of water from atomic reactor installations, research organizations, or hospitals has emphasized investigations of methods of dealing with such contamination.

Removal of radioactive contaminants from water by ion exchange slurry is among the latest of these methods tested by the Sanitary Engineering Branch of the Corps of Engineer's Research and Development Laboratories, Fort Belvoir, Virginia.

The method consists in removing the radioactive contaminants from the water by the addition of commercially available ion exchange resins. Attracted to the resins, the radioactive ions settle out with them after the solution has been agitated.

★A department of metallurgical engineering has been established in the New York University College of Engineering, Dean Thorndike Saville announced. Acting chairman of the new department will be Dr. John P. Nielsen. "Increasing interest and specialization in metallurgy on the undergraduate, graduate, and research levels warrants the creation of a separate unit for metallurgical engineering in this college," Dean Saville said.

This brings to 12 the number of departments in the College. The last new one, the department of meteorology and oceanography, was created in 1937.

★The five eastern warehouses of Will Corporation and subsidiaries have been appointed distributors of Metalab's complete line of SD-3 sectional laboratory furniture. If you are planning a new laboratory or a re-arrangement of your present one, write for free catalogue and planning kit to Will Corporation, Rochester 3, N.Y.

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EACH	$ .25	.35	.40	.45	.65
DOZEN	$1.80	1.90	3.00	3.65	5.75
CAPACITY (oz.)	32	½ gal.	1 gal.	2 gal.	
NECK FINISH (mm.)	38	38	38	38	
EACH	1.20	3.95	5.00	9.65	
DOZEN	11.00	40.00	50.00	100.00	

S36-851 FUNNELS

Outside Diameter (in.)

Top	Top of Stem	Bot. of Stem	Stem Lgth.	Each	Doz.
3	7/16	5/16	3"	$1.00	$10.00
4	11/16	5/8	1 5/8"	1.25	12.50
6	13/16	5/8	3 1/4"	1.40	14.00
7¼	1	7/8	3 1/8"	1.50	15.00

S5-294/1 BEAKERS

Capacity ml.	30	70	100	150	200
Each List	.60	.70	.75	.80	.90
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Each List	.95	1.00	1.40	1.60	

S77-932 POLICEMEN

One end flattened with diagonally cut edge. Size 7" long, ¼" diam.—$.40 Each.....$3.60 per Dozen

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Same as Policemen but without flattened and diagonally cut end. Size 6¼" long, ¼" diam.

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S12-471 LIGHTWEIGHT CARBOYS

(with polyethylene Buttress Caps)

Capacity Gallons	Each	Lots of 6, Each	Lots of 12, Each
6½	$20.00	$19.00	$18.00
13	32.00	30.00	28.00

S12-472 JACKETED CARBOYS

Capacity Gallons	Lots of 1–2, Each	Lots of 3–5, Each	Lots of 6–12, Each
6½	$30.00	$27.00	$24.00
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25 ml	4.05	3.85 each
50 ml	4.15	3.75 each
100 ml	4.85	4.50 each
250 ml	5.35	5.00 each
500 ml	8.25	8.00 each
1000 ml	9.25	8.75 each

S7-128 WASH BOTTLES

Capacity (oz.)	Each	Lots of 3, Each	Lots of 12, Each
4	$ .90	$ .80	$ .63
6	1.00	.90	.70
8	1.10	1.00	.75
16	1.40	1.30	1.20
32	2.00	1.80	1.60

S17-824 POLYETHYLENE CENTRIFUGE TUBES 15 ML CAP.

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Various types of current observed in polarography (residual, absorption, migration, diffusion, kinetic and catalytic) are treated extensively and each is illustrated by simple experiments which can be carried out in any student laboratory. Dr. Müller shows how to distinguish between these types of currents and how to recognize diffusion, kinetic and catalytic currents by varying the drop-time or -size of the mercury electrode.

The author has presented a new approach to the problem of polarization of an electrode which may have some value for student instruction. Detailed discussion of this problem includes directions for testing the non-polarizability of an electrode.

Rather than enumerate a number of detailed analytical procedures, Dr. Müller has given the principles on which these are based, with sufficient instruction to enable anyone to develop his own, or carry out a published analytical procedure. Following the given directions, no one should find it difficult to test the polarographic reversibility of a reaction or to determine the coordination number of a complex metallic ion.

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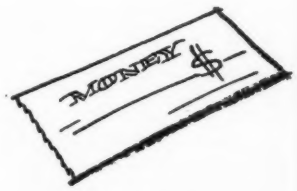

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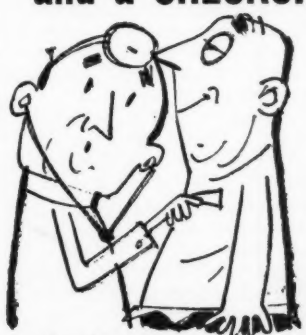

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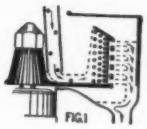

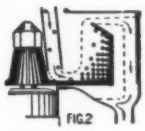

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For Non-hazardous Locations

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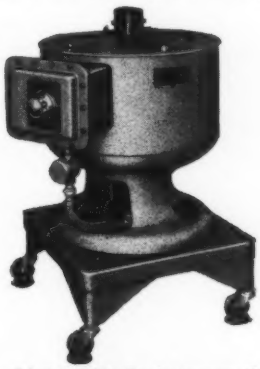
Basket Dia.	*Cake Cap.*	*Max. R.P.M.*	*Max. Force*
5 inch	300 ml.	4000	1130 x G.
8 inch	1500 ml.	3500	1390 x G.
11 inch	3000 ml.	3500	1900 x G.

A total of 39 other heads for centrifuging material held in tubes or bottles (10 to 600 ml. capacity) are also usable on the Model U Centrifuge.

Model BE50 Centrifuge — 5, 8 and 11 Inch Baskets

For Class I, Group D Locations



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Interchangeable solid or perforated baskets available in bronze or stainless steel (other materials to order). The centrifuge can be operated continuously until the cake capacity of the basket is reached. Operating capacities and characteristics of the various sized baskets are as follows:

Basket Dia.	*Cake Cap.*	*Max. R.P.M.*	*Force*
5 inch	300 ml.	3500	870 x G.
8 inch	1500 ml.	3500	1390 x G.
11 inch	3000 ml.	3500	1900 x G.

A total of 32 other heads for centrifuging material held in tubes or bottles (10 to 600 ml. capacity) are also usable on the Model BE50.

Size 3, Model FS — 14-Inch Baskets

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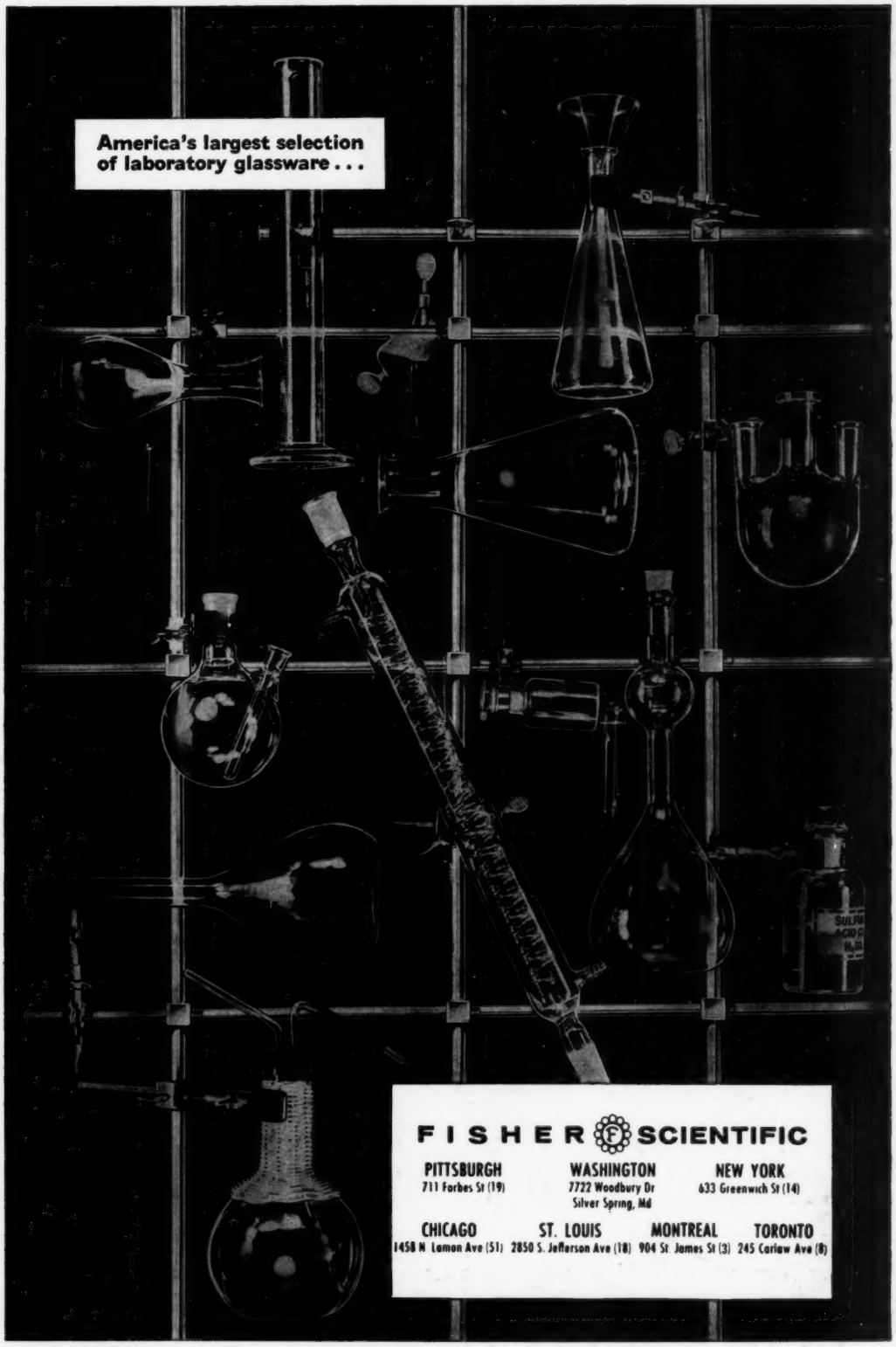
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